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ON THE PEROXIDES AND SO-CALLED DOUBLE HALIDES.

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The double salts formed by the interaction of the halides of the alkali metals with those of the other metals generally, constitute an important and ever-growing class of substances which seem fully to deserve the qualification *homogeneous*.

If we except the recognition of the fact that the maximum number of molecules of alkali halide with which a given metallic halide interacts, is as a rule determined by the number of halogen atoms in the molecule of the metallic halide, we may say that the study of this class of bodies has not as yet resulted in any generalisation of importance.

While most chemists, to judge from the method of formulation usually adopted, seem to be in favor of the view that these double halides are representatives of the ill-defined and artificial class of molecular compounds, others maintain that they are true atomic compounds which owe their existence to the activity of the "residual affinities" of the chlorous atoms involved.

With regard to the former view, we fail to find any elucidation at all in the statement—double halides are molecular compounds. The inertia of scientific exploration is so great that it does not admit of any stoppage longer than is necessary to give more than a cursory glance at what is passed. If the nature of the phenomenon is not wholly revealed by this passing inspection, it is

relegated to a suspense-class for subsequent and more thorough investigation. It seems to us that the so-called molecular compounds constitute a suspense-class of this kind, which for convenience has received a mere name as distinguished from a connotation.

The explanation in terms of "residual affinities" is most gratuitous. Even were it preceded by a satisfactory description of the nature of an "affinity," it could not be regarded otherwise than as an ingenious and expiring effort of a theory now well to the west of its meridian. The admittance of the existence of residual affinities would in a measure account for the mere percentage compositions of a goodly number of the double halides, but it would at the same time most certainly lead us to wrong conclusions respecting their constitutions. If there is, as every one will we think readily admit, a universal correlation between structure and properties, then according to the doctrine of residual affinities the product of the interaction of $3KCl$ and $SbBr_3$ ought to differ in its behavior from the product of the interaction of $3KBr$ and $SbCl_3$. For the atom linking is different in the two cases. In both cases, according to the advocates of residual affinities, there is direct interaction between the bromine and chlorine atoms, but in the former case the chlorine atoms act only indirectly on the antimony atom, whereas in the latter case this action is direct. It is, however, a well ascertained fact that the products of the interaction of $SbCl_3$ and $3KBr$ on the one hand and $SbBr_3$ and $3KCl$ on the other, are identical.[1] Similarly the same body results from the interaction of TlI_3 and KI, as from the interaction of TlI and KI_3.[2]

Recently Mendeléeff[3] read a paper before the Royal Society in which he showed how the numerous carbon compounds, isomerides included, can be adequately represented quite independently of the valence theory and as a simple consequence of the application to the atomic constituents of molecules of Newton's Third Law of Motion in the form in which it appears when regarded as a corollary of the First Law. If the latter be true, then the internal stresses of any system must of necessity form a complete and mutual balance. This Law, coupled with a most plausible assumption, Mendeléeff introduces into chemistry under the title of the "Principle of Substitutions," which he illustrates much as follows:

[1] Atkinson: J. Chem. Soc. **43**, 290. [2] Johnson: *Ibid.* **33**, 183. [3] Nature 1032, 354.

Let ABC and AD represent two molecules; then since the interatomic stresses in these two molecules cannot have resultants, according to Newton's Third Law of Motion, it follows that the partial stress exerted (in some obscure way, in virtue, perhaps, of oscillatory or orbital motions) by A on BC is equal to the counter partial stress exerted by BC on A; that similarly the partial stress between A and D is exactly equal and opposite to that between D and A. Then comes the assumption—Mendeléeff calls it an axiom—which virtually states that the stress an atom exerts is constant for that atom; from which it follows at once that DBC will be a system in dynamic equilibrium, and therefore capable of existence.

It is the object of this paper to apply Mendeléeff's suggestion to what is known of the true peroxides[1] and double halides; and the outcome of this application, stated briefly, is that the members of this particular class of so-called double salts appear in the light of what by analogy may be called perhalide forms, bearing to the normal halides much the same relation as the true peroxides bear to the ordinary Group-oxides.

In dealing with the constitution of the peroxides, or rather their mode of derivation from the Group-oxides of Mendeléeff in terms of Newtonic principles, let us first briefly consider the simplest peroxides known, *viz.* those of hydrogen and potassium, and then pass on to those of Mendeléeff's eight Groups taken in order.

We might at first be inclined to regard hydrogen peroxide as derived from the water molecule H.OH by the substitution of the H atom of the hydroxyl group by hydroxyl itself, since, from the very fact of the existence of water, H and OH must be dynamically equivalent in the Newtonic sense. But on applying this mode of derivation to other stable hydroxides we get peroxides of higher degrees of oxidation than either are known to exist, or are probable. Thus sulphuric acid would yield the two peroxides SO_4 and SO_5; barium would form peroxides having the formulæ BaO_2 and BaO_3, whilst the lowest possible peroxide of potassium would be K_2O_3. Since, however, the highest known unequivocal peroxides of barium and sulphur have, respectively, the formulæ BaO_2 and S_2O_7, and the lowest peroxide of potassium is K_2O_2, it follows that we must reject unconditionally the view that peroxides may

[1] Mendeléeff has already made an incomplete application of his principle to a few of the better known peroxides.

empirically be regarded as formed by replacing the hydrogen atoms of the hydroxyls of the Group-hydroxides by hydroxyl, with subsequent dehydration.

But hydrogen peroxide may be derived from water in another way, which, although conducing to the same empirical result in the particular case of hydrogen peroxide as does the former method of attacking the problem, yet gives quite different results in the cases of the other peroxides.

Instead of conceiving a direct substitution of the hydrogen atom of the hydroxyl group by another hydroxyl group, let us glance at the results of supposing the hydrogen atom of the hydroxyl group substituted by the atom-complex constituted by all the remaining atoms in the molecule—a sort of reduplication or partial polymerisation with or without the elimination of water.

The application of this principle to the water molecule gives of course HO.OH. But there is no good reason for distinguishing between the hydrogen atoms in the water molecule, or for the assertion that one rather than the other is a constituent of the hydroxyl radicle. Hence it is probable that an elimination of one of the hydrogen atoms of hydrogen peroxide attended with a reduplication, will some day be realised in the isolation of a body H_2O_4[1] corresponding to its well known potassium analogue, K_2O_4.[2]

If we apply this principle of the derivation of the peroxides to what little is as yet known about the peroxides of the remaining Groups of the Periodic System, we find a close agreement between fact and deduction.

Hydroxides of Group II are of the type $M(OH)_2$. Hence peroxides of the elements of this group should exist of the types

$$M<\begin{matrix}OH & HO\\ O & O\end{matrix}>M \quad \text{and} \quad M<\begin{matrix}O.O\\ O.O\end{matrix}>M.$$

[1] Thénard and Berthelot are of the opinion that a peroxide of hydrogen of higher type than H_2O_2 is formed when $KMnO_4Aq$ and H_2O_2 interact at low temperatures.

[2] This form of reduplication seems to take place also in the case of hydrates of lower oxides than the highest Group-oxide. Thus P_2O_4 is the anhydride of hypophosphoric acid derived thus from phosphorous acid:

$$P(OH)_2O.H + P(OH)_2O.H \text{ gives } \begin{matrix}P(OH)_2O\\ P(OH)_2O\end{matrix} \text{ or } H_4P_2O_6.$$

Sulphurous acid by the same method yields hyposulphuric acid, $H_2S_2O_6$, the anhydride of which is the alleged S_2O_3. S_2O_3 would be the anhydride of the reduplicated acid H_2SO_3 which Schützenberger thought to have prepared. Similarly N_2O_4 is derivable from nitrous acid. It is characteristic of all the oxides thus derived that they react with water to form, not the acids of which they are theoretically the anhydrides, but mixtures of other acids.

As representatives of the first type we have the bodies $Zn\overset{OH}{\underset{O}{}}\!\!\overset{HO}{\underset{O}{}}Zn$ and $Cd\overset{OH}{\underset{O}{}}\!\!\overset{HO}{\underset{O}{}}Cd$, usually written $Zn(OH)_2ZnO_2$ and $Cd(OH)_2CdO_2$ respectively. The well known peroxides of the alkaline earth metals are representative of the second type.[1]

The hydroxides of elements of Group III are of the general form $M(OH)_3$; these elements, in accordance with our views, should form peroxides having the empirical formulæ M_2O_4, M_2O_5 and M_2O_6. In the case of thallium, Tl_2O_4 is known in a state of combination; and the only other known peroxides of this group are the little-investigated bodies Y_4O_9 and La_4O_9.[2]

Peroxides of the elements of Group IV should exist having the compositions M_2O_5, M_2O_6, M_2O_7 and M_2O_8. Three of these types have known representatives in the bodies Zr_2O_5, Te_2O_6, Ce_2O_6, $Sn_2O_6.H_2O$ (?) and Th_2O_7.

Since the highest stable hydroxide of Group V is $MO(OH)_3$ —*i. e.*, $M(OH)_5$—H_2O,—the elements of this group should show

[1] It does not seem to have been incontrovertibly proved that barium dioxide is produced when the monoxide is heated in oxygen, text-books to the contrary notwithstanding. Brodie's results (Phil. Trans. 1850) seem to be the only quantitative ones in this connection, and they are not quite satisfactory. When the monoxide passes over into the peroxidised form, BaO_2, there should be a percentage increase of 10.5; whereas Brodie only found 7.56. Conversely, when the peroxide passes to normal oxide there should be a percentage loss of 9.5. Brodie found only 6.78. It should be here noted that the product of the interaction of barium oxide and potassium chlorate at a red heat is, according to Berthelot, not BaO_2 but Ba_2O_3, the dehydrated form of the first type $M\overset{OH\ HO}{\underset{O.O}{\diagdown\diagup}}M$. Thénard, the discoverer of a peroxide form of barium, had no quantitative analytical results, but merely conviction to adduce in favor of the formula BaO_3 (Ann. chim. phys. [2] **8**, 308).

[2] Besides the peroxide forms deduced by the principle enunciated above, it seems necessary to admit others of intermediate type. Thus in addition to the two peroxides of potassium, K_2O_3 and K_2O_4, oxides having the compositions K_2O_2, K_4O_3, K_8O_4 and K_8O_5 have been described. Barium has also a peroxide form of the composition H_2BaO_4. Hitherto it has been customary to regard most of these bodies as "molecular compounds" of two oxides rather than as true atomic compounds. In accordance with this conception, these bodies are generally represented thus: $K_2O_3.K_2O=K_4O_3$; $K_2O_3.2K_2O=K_8O_4$; $K_4O_3.3K_2O=K_8O_5$; $BaO_2.H_2O_2=H_2BaO_4$. But they can be represented equally well in terms of Mendeléef's substitution theory without involving the idea of molecular combinations between peroxides, or between peroxides and normal oxides. Thus from BaO_2 we derive by substitution $Ba(OH)_2$ or $Ba(OH)O.H$. This in reacting with H_2O_2 or $(HO)O.H$, in accordance with Newtonic principles, gives $\left.\begin{matrix}Ba(OH)O\\(HO)O\end{matrix}\right\}$ or $BaO_2.H_2O_2$. The peroxide K_2O_3 may be similarly derived from K_2O_2 and H_2O_2, only in this case the reduplication is followed by dehydration. From the simultaneous existence of the compounds K_2O_3 and K_2O_2 we can predict the existences of the remaining peroxides of K. The peroxides M_4O_9 of Group III may in like manner be regarded as derived from what may be called the normal peroxides $M_2O_5[M_2O_4.O]$ and $M_4O_8[M_2O_4.O]$ thus: $\left.\begin{matrix}M_2O_4\\M_2O_5\end{matrix}\right\}$. The only objection is that this method of derivation does not seem to point to any limit in the number and complexity of the peroxides of a given element.

representatives of the types M_2O_6, M_2O_7 and M_2O_8. As yet, however, the only known peroxide of this group is N_2O_6.

The application of our principle to the stable hydrates of the Group-oxides of Group VI, $MO_2(OH)_2$, *i. e.* $M(OH)_6—2H_2O$, demands peroxides of the types M_2O_7 and M_2O_8.

The elements of this group show themselves particularly prone to the formation of peroxide forms, among which we may note S_2O_7 (both as anhydride, and in combination with bases as salts), Cr_2O_7 (?), Mo_2O_7 and W_2O_7 (both in combination with alkalies) and $UO_4.4H_2O$. The peruranates[1] of Fairley may most simply be regarded as hydrated bodies belonging to the same category as Schöne's H_2BaO_4 (see note 2, p. 5), *i. e.*, compounded peroxides formed in conformity with the substitution principle. Thus $Na_4UO_8.4H_2O = UO_4.2Na_2O_2.4H_2O$. Last year Traube[2] asserted that he had proofs of the existence of an oxide of sulphur SO_4, analogous in composition to the uranic peroxide just mentioned. But his proofs are not at all satisfactory,[3] and although according to the principles here developed SO_4 is a legitimate object of research, it seems as if Traube's sulphur holoxide were nothing else than Berthelot's persulphuric anhydride, S_2O_7.[4]

[1] A thorough and more detailed investigation of these peruranates, and of peroxides generally, is much to be desired. More attention must henceforth be devoted to the determination of their constitution. There are many chemists who write $UO_4.4H_2O$ and $Na_4UO_8.4H_2O$ in the forms $U_2O_7.H_2O_2.7H_2O$ and $UO_8.2Na_2O_4H_2O$ respectively, with no better apparent reason for their procedure than that there is no room in their own private philosophies for bodies of the constitutions implied in the former formulæ. In terms of the idea of molecular compounds these methods of representation directly imply the existence of oxides U_2O_7, UO_8 and UO_4. The representation of a body in terms of the substitution principle does not in any way suggest the integral presence in the body of the constituents by whose interaction the body is presumably formed. Thus Fairley's peruranate, $Na_4UO_8.4H_2O$, regarded as the product of the interaction of $U(OH)_8$ [$= UO_4.4H_2O$] and $Na_2(OH)_2$ [$= Na_2O.H_2O$] would be represented thus: $\left.\begin{matrix}Na_2(OH).O\\U(OH)_4.O_2\\Na_2(OH).O\end{matrix}\right\}$.—See note 2, p. 5.

The other sodium peruranate described, *viz.* $Na_2U_2O_{10}.6H_2O$, may be regarded as similarly derived from $U_2(OH)_{14}$ [$= U_2O_7.7H_2O$] and $Na_2(OH)_2$ thus: $\left.\begin{matrix}U_2(OH)_{12}O_2\\Na_2O_2\end{matrix}\right\} = Na_2U_2O_{10}.6H_2O$.

[2] Ber. d. chem. Ges. **24**, 1764.

[3] See Berthelot: Comp. rend. **112**, 1481; also Carnegie: Chem. News **64**, 266.

[4] It has recently been stated (J. Chem. Soc. **59**, 785) that "the only result given by Traube which points to the possibility of such a substance (SO_4) being present in the oxidised liquid, is that showing the ratio of oxidising power to sulphuric acid formed on decomposition; the H_2SO_4 previously present having been removed by means of barium phosphate." But it seems to me that this ratio may be fully accounted for in terms of the equation of decomposition—

$$K_2S_2O_8\,[=S_2O_7.K_2O] + H_2O = 2KHSO_4 + O$$

if we recall that it was *acidity* and not total sulphuric acid that Traube estimated.

The peroxides of Group VII should conform to the type MO_4, but as yet no peroxides of this group have been isolated.[1]

If considerations of symmetry and general plan are worth anything—and surely the results of reasoning based on the Periodic Law show that they are—then we are led to the conclusion that the elements of Group VIII will not form true peroxides. The highest stable hydrates of the oxides of elements belonging to Groups V, VI and VII are obtained by abstracting the elements of one, two and three molecules of water respectively from what we may call the orthohydroxides of these groups, in accordance with the following scheme:

Group	V.
Orthohydroxides,	$R(OH)_5$.
Stable hydrates,	$R(OH)_5 - H_2O = RO(OH)_3$.
Group	VI.
Orthohydroxides,	$R(OH)_6$.
Stable hydrates,	$R(OH)_6 - 2H_2O = RO_2(OH)_2$.
Group	VII.
Orthohydroxides,	$R(OH)_7$.
Stable hydrates,	$R(OH)_7 - 3H_2O = RO(OH)$.

Extending this regularity to Group VIII, *i. e.*, abstracting the elements of four molecules of water from its orthohydroxide, $R(OH)_8$, the result is a body altogether free of hydroxylic hydrogen, and therefore not amenable to the principles of peroxide derivation here developed. In strict conformity with these considerations we find that RuO_4 and OsO_4 are not only incapable of combining directly with water to form definite hydrates, but that their solutions in water do not exhibit any acid characteristics whatever.

It is worthy of note that this method of regarding the peroxides leads us to a conclusion which, though its significance is not yet very clear, has been repeatedly emphasised by Mendeléeff both in his Faraday Lecture of 1889, and in various connections in his "Principles of Chemistry," *viz.*, that a binary molecule *never* contains more than *four* atoms of oxygen per atom of the other constituent element.

[1] Franke thought to have prepared a peroxide of manganese MnO_4 in the form of a blue gas, but Thorpe and Hambly, following Franke's directions, were unable to obtain any evidence of a peroxide of manganese.

What, in conclusion, it may be asked, is the definition of a peroxide?

We would suggest, in answer, that all oxides of any given element with higher percentages of oxygen than the highest Group-oxide of the element according to Mendeléeff, are true peroxides.[1] Mendeléeff to the contrary, such peroxides may be possessed of truly basic or acidic properties; some may even be anhydrides. Thus, S_2O_7 is the anhydride of an acid $H_2S_2O_8$ which forms salts (isolated by Marshall) by replacement of the two hydrogen atoms by metals. The same, according to Péchard, is true of Mo_2O_7 and W_2O_7.[2] Other peroxides such as UO_4 do not appear to be truly anhydrides—that is, they do not form hydrates with replaceable hydrogen. Yet they have something akin to acid properties, in virtue of which they form compounds with the peroxides of the more basylous metals. When one recollects that it is impossible sharply to differentiate such classes as metals and non-metals, acids and bases, etc., it is not to be wondered at that the diagnosis of peroxides from their properties alone is not a sharply defined one. As a class they may be said to be less stable at high temperatures than the normal oxides. They are for the most part decomposed by water and very dilute acids, and it is probable that a more careful examination of these decomposition-products will in all cases disclose the presence of hydrogen peroxide. Many of these bodies when treated with concentrated sulphuric or nitric acid disengage ozonised oxygen, and this reaction is very probably a distinctive reaction of the class.

Before passing on to the so-called double halides formed by the alkali metals, we must first glance at the perhalide forms of the alkali metals themselves.

From the molecules KO.H and HO.H we get, by the principle of substitutions, KO.OH in which the oxygen atoms bear the same relation to each other that they do in peroxide of hydrogen. They may therefore be substituted by two hydrogen atoms giving us KH.HH. But the hydrogen atom is equivalent from a substitution point of view to a halogen atom, say I; and thus we arrive at the well known triiodide of potassium, KI_3. Although

[1] Hence PbO_2, MnO_2 and CrO_3 are not true peroxides.

[2] Cammerer (Chem. Zeit. **15**, 957) accepts the formula $2MoO_3.H_2O_2.xH_2O$ in preference to Péchard's formula $H_2Mo_2O_6.xH_2O$. Cammerer has also isolated a peroxide of tungsten which he represents as $WO_3.H_2O_2.H_2O$. But there seems to be no good reason why it should not be represented as a hydrate of the theoretically-possible tetroxide, $WO_4.2H_2O$.

solubility-data point to the probable existence of analogous bromine and chlorine compounds of potassium, these have not yet been isolated. Quite stable bodies of the type MX_3 (where X is any halogen) have, however, recently been described where M is cæsium.

From the existence of a chloride of iodine having presumably the molecular formula ICl_3, still higher perhalide compounds of the alkali metals are possible, and are known. By the principle so often employed already, $KI_3.I + Cl_2.I$ points to the existence of a body $KI_3.Cl_2$, or in general to bodies of the type KX_5. Wells and Wheeler have described, among others, the following substances conforming to this type: CsI_5, $CsBr_5$, $KCl.Cl_3I$, $LiCl.Cl_3I$.

Since, however, of the three iodine atoms in KI_3 two bear necessarily a similar relation to the system, no reason exists why a further substitution should not take place between the two molecules KI_3Cl_2 and ICl_3 giving us (say) $KICl_2.Cl_3$, or in general a body of the type KX_7. Such a body is known in the double fluoride KH_3F_4—usually written $KF.3HF$. It must be noted that no double halide of alkali metal and hydrogen of higher type than this is known.

Passing on now to the elements of Group II, whose stable hydroxides are of the form $M(OH)_2$. By the substitution principle,

$$M\overset{OH}{\underset{O.}{}}H + KO.H \text{ gives } M\begin{matrix}OH\\O\\KO\end{matrix}\Big\}.$$

This by reason of the existence of $\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ gives $M\begin{matrix}OH\\H\\K\ H\end{matrix}\Big\}$, and this MX_3K, where X is any halogen atom, and M an element belonging to Group II. Of the many bodies conforming to this type we shall take the single example $MgF_3.NaF$.

$$\text{But } M\begin{matrix}O.H\\H\\KH\end{matrix}\Big\} + KO.H \text{ gives } M\begin{matrix}KO\\O\\H\\KH\end{matrix}\Big\}; \text{ and this, as before, } M\begin{matrix}KH\\H\\H\\KH\end{matrix}\Big\} \text{ or}$$

MK_3X_4. Again we shall take but one example of the many bodies of this type, $BeCl_2.2KCl$.

Finally, by four successive substitutions on Newtonic principles between MK_3X_4 and the halide atoms of 4 molecules of KX_3—one atom from each molecule—we arrive at the perhalide types MK_3X_5, MK_4X_6, . . . MK_6X_8. As yet, however, representa-

tives of only the first two types are known—*e. g.*, $ZnCl_2.3NH_4Cl$; $CdCl_2.4KCl$. It would seem therefore that higher perhalide forms of the elements of Group II remain to be discovered.

Similar reasoning applied to Group III leads to the following gamut of perhalide types for the elements of this group:

MKX_4	$AlCl_3.NaCl$
MK_2X_5	$AlF_3.2NaF$
MK_3X_6	$AlF_3.3NaF$
MK_4X_7	...
MK_5X_8	$TlI_3.5TlI$[1]
.	
.	
.	
MK_9X_{12}	...

Group IV is especially rich in perhalide compounds, which according to theory should range between the limits MKX_5 and $MK_{12}X_{16}$ for the "-ic" salts, and the limits MKX_3 and MK_6X_8 for the "-ous" salts.

MKX_5	$ZrF_4.KF$
MK_2X_6	$ThF_4.2KF$
MK_3X_7	$TiCl_4.3NH_4Cl$
MK_4X_8	$[ZrF_4.2CdF_2]$
MK_5X_9	...
MK_6X_{10}	$TiCl_4.6NH_4Cl$
MK_7X_{11}	...
MK_8X_{12}	$ThCl_4.8NH_4Cl$
MK_9X_{13}	$PbCl_4.9NaCl$
.	
.	
$MK_{12}X_{16}$	...
MKX_3	$SnBr_2.KBr$
MK_2X_4	$PbI_2.2KI$
MK_3X_5	$PbI_2.3NH_4Cl$
MK_4X_6	$PbI_2.4KI$[2]
MK_5X_7	...
MK_6X_8	$PbBr_2.6NH_4Br$.

[1] The thallium atom is, we know from the existence of thallous compounds, substitutionally equivalent to the atom of an alkali metal.

[2] Doubt has been thrown on the existence of Boullay's $PbI_2.4KI$ by Remsen and Herty: This Journal **11**, No. 5; **14**, No. 2.

In connection with the double halides formed by the plumbous salts occurs the only discrepancy between theory and actuality that we have met in the course of this review. According to theory, MK_6X_8 should define the limit for plumbous perhalides, and all perhalides of higher type than MK_4X_6 we would expect to be quite unstable. But André claims to have separated homogeneous and fairly stable compounds having the empirical formulæ $PbX_2.7NH_4X$ — $PbX_2.10NH_4X$. This discrepancy merits a more careful experimental investigation.

The elements of Group V form very few perhalide compounds; the known representatives are all of low type, and fall well within the limits assigned by theory—*e. g.*, $BiCl_3.2NaCl$; $BiCl_3.3NH_4Cl$; $BiCl_3.4NH_4Cl$. Scarcely anything is known concerning the double alkali halides formed by the more basic elements of Group VI; and the important perhalides of the elements of Group VIII are all normal, but of very low type.

A review of these perhalides and their mode of derivation suggests a subdivision into three groups, *viz.*, perhalides of the first, second, and third orders.

To the first order belong those perhalides which, from a molecular-compound standpoint, do not contain a greater number of molecules of alkali halide than the number of halogen atoms in the molecule of the other metallic halide involved. To this order belong such bodies as $MgF_2.NaF$ and $BeCl_2.2KCl$. The ability to form the limit-compounds of this order is possessed in higher degree by the elements of the lower groups than by those of the higher. Of the many important perhalides formed by the tetra-halides of the metals of Group VIII—the platinum group of metals—none reach the limit form $MX_4.4KX$.

The second order is composed of those perhalides which may be regarded as containing a number of alkali halide molecules anywhere between the number limiting the first order and double that number—*e. g.*, $ZnCl_2.3NH_4Cl$; $CdCl_2.4KCl$.

Finally, the third order comprises those perhalides which contain a number of alkali halide molecules ranging between the number limiting the second order and three times the number limiting the first order. Such, for instance, are the bodies $BaCl_2.5KCl$ and $BaCl_2.6KCl$ yet to be discovered. Group IV, however, furnishes us with an example of this order in the body $PbBr_2.6NH_4Br$.

It is particularly noteworthy that the great majority of the known perhalides belong to the first order, and that ammonium halides seem more prone to form perhalides of higher orders than do the halides of the alkali metals. Or at least we may say that as the order rises the stability of the perhalide decreases, but that this decrease of stability appears to be less for the ammonium halides than for the alkali metal halides.

In addition to the perhalides already noticed in this paper, numerous intermediate, or poly-, halides are possible and are known to exist—*e. g.*:

$2CeF_3.3KF$; $2BiI_3.3NaI$; $3MoCl_4.2KCl$; $2HgCl_2.KCl$, etc.

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ON THE LIBERATION OF NITROGEN DURING PUTREFACTION.

BY HOWARD B. GIBSON.

Historical.—The study of the conditions and processes which affect the supply of combined nitrogen has been a very fruitful one, and the brilliant researches which led to the discovery that the leguminæ utilise free nitrogen by a process of symbiosis with certain micro-organisms, are too widely known to need more than passing notice. While the supply of combined nitrogen may be increased in this way, and probably in others, there are also processes continually going on by which combined nitrogen passes into the free state; among them may be mentioned the use of our modern explosives, the combustion of organic nitrogenous substances, and the action of certain micro-organisms in the process of putrefaction.

The study of the liberation of nitrogen during putrefaction was begun by Rieset[1] in 1856, and has been continued until the present day with very varied results. Between 1856 and 1882 Lawes, Gilbert and Pugh,[2] in England, and Koenig,[3] Morgen,[4] Dietzell,[5] and Gautier and Etard,[6] in Germany and France, conducted

[1] Compt. rend. 1856, 63.
[2] Phil. Trans. Lond. 1861, 497.
[3] Der Kreislauf des Stickstoffs, Münster, 1878.
[4] Landw. Vers.-Stat. **30**, 199.
[5] Ber. d. chem. Ges. **16**, 551.
[6] Compt. rend. **94**, 1357.

experiments which showed that liberation of nitrogen may take place. Since 1882 experiments by Ehrenberg,[1] Tacke,[2] Kelner and Yoshii,[3] Schlösing,[4] and Berthelot and André[5] have given negative results, while in further researches by Tacke[6] and also by Immendorff[7] positive results have been obtained.

In these experiments two general methods have been followed: the "difference" method, in which the nitrogen in a definite amount of substance is determined before and after putrefaction; and the "gas-analysis" method, in which the gaseous products of putrefaction are examined for the presence of nitrogen gas. Both methods, as formerly used, are open to criticism, the former because of the possibility of the passage of indol, skatol, etc., through the solutions used in absorbing the ammonia gas formed during putrefaction, and of the loss of volatile nitrogenous substances while drying the residue preparatory to analysis; and the latter because the conditions of experiment are apt to be abnormal. The absence of the details of much of the work previous to 1882, in which the "difference" method was almost exclusively used, makes it impossible to estimate the extent to which errors of method may have influenced results, but in much of the work by the "gas-analysis" method the conditions of experiment have been such as to render results of a very questionable nature.

The classification of such a mass of results along definite lines is difficult, especially in the case of the work previous to the last five years; but in the more recent work, with a single exception observed by Immendorff, no losses of nitrogen have occurred when nitrates have not been found present at the end of the experiment, although the presence of nitrates has often been observed when no liberation of nitrogen has taken place. Two principal theories have been advanced in explanation of the liberation of nitrogen. The older one, adopted by Koenig and Morgen, was that the ammonia formed in putrefaction was oxidised to nitrogen gas and water in a manner analogous to the decomposition of ammonia gas by chlorine. In the later theory the liberation of nitrogen has been associated with the process of nitrification, in connection with which, as mentioned above, the liberation of nitrogen has been observed. The evidence as to a direct con-

[1] Ztschr. physiol. Chem. **11**, 145, 438. [2] Landw. Jahrb. **16**, 917.
[3] Ztschr. physiol. Chem. **12**, 95.
[4] Compt. rend., **108**, 261; Ref.—Centrbl. Agr.-Chem. 1889, 218.
[5] Compt. rend. **114**, 514. [6] Landw. Jahrb. 1889, 39. [7] *Ibid.* 1892, 281.

nection between the two processes seems to be negative. Neither Ehrenberg[1] nor Schlösing[2] observed liberation of nitrogen during the nitrification of ammonium salts in presence of oxygen.

Dehérain[3] observed a loss of nitrogen in soil in which nitrification was going on, but he did not refer the loss to nitrification itself, as the loss did not occur until the intensity of the nitrification process had begun to decrease. Tacke's[4] experiments by the difference method showed gain as well as loss of nitrogen where nitrification had taken place, and Immendorff[5] observed a loss in all cases when nitrification had gone on, but failed to discover any quantitative relation between nitrification and loss of nitrogen. Leone[6] observed the reduction of nitrates by micro-organisms, and E. Bréal[7] has found an aerobic ferment which reduces nitrates to free nitrogen.

This evidence as a whole, and especially the observations of Leone and Bréal, seems to indicate that the liberation of nitrogen is a process independent of nitrification.

In two of Immendorff's experiments heavy losses of nitrogen occurred without either nitrates or nitrites being present at the end of the experiments. There is nothing in this experimental work, however, which debars the possibility of previous nitrification and reduction, but Immendorff takes the ground that liberation of nitrogen may be caused by the action of micro-organisms independent of the process of nitrification. Although Immendorff's experimental work may not entirely justify his conclusions, the writer believes this theory is correct, and offers his own experimental work as proof that the liberation of nitrogen may take place during putrefaction, without the previous formation of either nitrates or nitrites.

Method.—In the experimental work herewith reported, simplicity of method was the end ever kept in view. The "difference" method was used, and the substance experimented upon was allowed to putrefy in glass bell-jars varying in size from one to three liters, and was placed in small watch-glasses arranged on metal stands. As none of the portions in the several glasses exceeded one gram in weight, the access of air to the putrefying mass was much freer than would have been possible had the substance been in a single large portion. Washed air was passed

[1] Ztschr. physiol. Chem. **11**, 446.
[2] Compt. rend. **109**, 423.
[3] Centrbl. Agr. Chem. 1887, 728.
[4] Landw. Jahrb. 1879, 39.
[5] *Ibid.* 1892, 281.
[6] Centrbl. Agr.-Chem. 1890, 283.
[7] Compt. rend. **114**, 681.

through the jars—as a rule every day—at the rate of about 4 bubbles per second. The average daily quantity of air thus passed through each jar was approximately equal to twice its capacity. Before admission to each jar the air was thoroughly washed by dilute aqueous solutions of caustic soda and sulphuric acid in order to remove all traces of nitric or nitrous acid and ammonia which it might contain. On leaving the bell-jar the air was made to pass, in the experiments of Series 1, through a dilute solution of sulphuric acid to absorb the ammonia formed during putrefaction; and, in Series 2, through concentrated sulphuric acid to absorb indol, skatol, etc., as well as ammonia.

The substances under treatment were lean beef and blood serum which in air-dried condition showed approximately the following composition:

Lean beef.—Water, 4.8; ash, 4.2; ether extract, 15.2; nitrogen, 12.0 per cent.

Blood serum.—Water, 10.7; ash, 10.0; nitrogen, 11.8 per cent.

The nitrogen content was carefully determined at the beginning of each experiment and, at its close, that of the several residues, which were transferred directly to the Kjeldahl digester without drying. Comparison of the original nitrogen content with that of the several residues *plus* the nitrogen found in the absorption-apparatus and water with which the jar and its fixtures had been carefully washed at close of experiment, showed whether liberation of nitrogen had taken place.

Error.—The errors especially guarded against were introduction of combined nitrogen in the air used in ventilation, loss of indol, skatol, etc., and leakage. As stated above, the air was thoroughly washed before admittance to the jars. In Series 2, indol, skatol, etc., were held back by the use of concentrated, instead of dilute, sulphuric acid in the absorption-apparatus, which was heated from time to time to decompose the absorbed gases. It was found that the use of concentrated acid prevented the escape of ill-smelling gases, which was very noticeable in Series 1, and discoloration of the acid was observed when the gases were allowed to pass through it on several successive days without heating. Each jar was carefully tested before each experiment and found capable of resisting a pressure from within equal to about 2 cm. of mercury. The use of a simple automatic device, however, excluded the possibility of pressure from within, and the possibility of error from leakage was thus practically excluded.

Although analytical errors are by no means a complete estimate of the error of a series of experiments of this kind, it may not be out of place to state that in the writer's use of the Kjeldahl method of nitrogen determination, which was used exclusively, the incidental error of titration rarely, if ever, exceeded 0.05 cc. of the alkaline solution, or less than 0.2 mg. of nitrogen. The probable error of the six series of determinations by which the original nitrogen content of the substances under experiment was found was ± 0.2, ± 0.1, ± 0.3, ± 0.3, ± 0.2, ± 0.4 mg. of nitrogen, respectively. Of the 34 individual determinations of the six series but a single one was rejected.

Conditions of Experiment.—The putrefaction was allowed to proceed in atmospheric air in very large excess of the actual amount necessary for the oxidation of the substance undergoing decomposition. No special effort was made to regulate the temperature at which the putrefaction took place, and the temperature of the laboratory ranged from 6° or 8° to 25°, and often changes of 12° or 15° occurred within 24 hours during the winter months. Distilled water was added to all portions of the substance at the rate of from 2 to 6 cc. of water per gram of substance. In Experiments 1–6 the putrefaction was started by addition of a drop of very dilute emulsion of putrid meat, and in Experiments 7–9 a couple of drops of dilute soil infusion were added in addition to the inoculation with the meat. With the exception of the manner of inoculation, all the experiments were carried on under approximately the same conditions. Neither the emulsion of meat nor the soil infusion contained a determinable amount of nitrogen per cc.

In the following table special attention is called to the loss per day both in milligrams, and in percentage of nitrogen taken, which brings out the following three points: (1) the comparative regularity of loss per day in Series 1; (2) smallness of loss in Experiment 6, in which, as in all experiments of Series 2, concentrated sulphuric acid was used in the absorption-apparatus, in comparison with losses in Series 1, where dilute acid was used; (3) difference in loss between experiments inoculated with soil infusion (7, 8 and 9) and the others.

The last column cannot be taken as an exact measure of the extent of the ammoniacal fermentation, as only total nitrogen was determined in the residues after putrefaction.

A Table summarising all Results.

Series.	Number.	Substance.	Inoculation.	Duration of Experiment in Days.	Nitrogen taken (in grams).	Nitrogen found (in grams).			Loss.				Nitrogen in Absorption-apparatus and Wash-water, in Percentage of Nitrogen taken.
									Total.		Per Day.		
						In Residue.	In Absorption-apparatus and Wash-water.	Total.	In Milligrams.	In Percentage of Nitrogen taken.	In Milligrams.	In Percentage of Nitrogen taken.	
1	1	Beef.	Putrid Flesh.....	63	0.6026	0.5058	0.0909	0.5967	5.9	1.0	0.09	0.016	15
1	2	Blood Serum	" "	167	0.5934	0.3372	0.2302	0.5674	26.0	4.4	0.16	0.026	39
1	3	" "	" "	168	0.5943	0.4031	0.1739	0.5770	17.3	2.9	0.10	0.017	29
1	4	" "	" "	87	1.0717	0.8383	0.2158	1.0541	17.6	1.6	0.20	0.018	20
1	5	Beef.	" "	98	1.0245	0.7456	0.2643	1.0099	14.6	1.4	0.15	0.014	26
2	6	"	" "	126	0.6057	0.5223	0.0762	0.5985	7.2	1.2	0.06	0.010	13
2	7	"	Putrid Flesh and Soil Infusion.	122	1.0283	0.4394	0.4350	0.8744	153.9	15.0	1.26	0.123	42
2	8	"	" " " " "	84	1.0334	0.7252	0.1865	0.9117	121.7	11.8	1.45	0.140	18
2	9	"	" " " " "	82	1.0290	0.7621	0.1682	0.9303	98.7	9.6	1.20	0.117	16

Theoretical Conclusions.—In Experiments 1, 4, and 5, a single representative portion, the nitrogen content of which was assumed from the average of the remaining ones, was tested for the presence of nitrates and nitrites by the starch-paste test, but with negative results. In Experiment 2, three portions, and in Experiment 3 all the portions, were tested by the diphenylamine test, but also with negative results.[1] In Series 2 each portion of each experiment was tested by the diphenylamine test, but not the slightest trace of nitrates or nitrites was detected. The possibility of nitrification and subsequent reduction is excluded, as Experiments 8 and 9 serve as control-experiments on Experiment 7 in the following manner: The duration of Experiments 8 and 9—84 and 82 days respectively—is only two-thirds that of Experiment 7—122 days—and, as the loss of nitrogen is directly proportional to the length of the experiment, therefore, if liberation of nitrogen had taken place at the same time with, or directly following, the nitrification process, nitrates would have been present in Experiments 8 and 9. Further, in each experiment the rate of putrefaction in the several portions varied very widely, so that the individual portions—of which there were 16 in each experiment—act as a control on each other and on the experiment as a whole. Bearing these facts in mind, the writer does not hesitate to assert that liberation of nitrogen without the previous formation of nitrates or nitrites may take place during the process of putrefaction as a result of the action of micro-organisms.

Summary.—1. Liberation of nitrogen may take place during the process of putrefaction.

2.—In the experiments reported, the liberation of nitrogen has been dependent on the inoculation, and certain micro-organisms (found in the putrid flesh) seem incapable of carrying on this process in any marked degree, while others (found in the soil infusion) have caused a marked loss of nitrogen.

3.—The micro-organisms have produced liberation of nitrogen independent of the process of nitrification.

In conclusion, the writer acknowledges his deepest obligation to the advice and kindness of his honored instructor, Professor Dr. F. Stohmann, under whose direction this research was carried on.

LEIPSIC, *June*, 1892.

[1] In the diphenylamine test the amount of substance required for the test was not large enough to be taken into quantitative consideration.

A STUDY OF CALIFORNIA PETROLEUM.

PRELIMINARY NOTICE.

BY FELIX LENGFELD AND EDMOND O'NEILL.

Petroleum occurs in many localities in California, most abundantly in the southern part, especially in Ventura and Los Angeles counties.

The industry has reached considerable proportions, the amount produced in 1888 being 704,619 barrels (of 42 gallons each[1]), and the annual yield is now probably much more than that amount.

The knowledge of its occurrence dates back many years; even as early as 1851 it was being distilled on a small scale, and in 1857 a comparatively large plant was erected in Santa Barbara county.

In 1865 there were 65 companies with a nominal capital of $45,000,000 engaged in the oil industry.[2] Interesting and full information on the subject is contained in the various reports of the California State Mining Bureau, especially those of 1884, 1887 and 1890. In spite of the above facts but little appears to have been done towards investigating the chemical nature of California petroleum.

In 1867 Silliman made rough analyses of some California oils, determining the specific gravity of a few fractions and giving the result of "cracking."[3] In 1887 W. C. Johnston determined the specific gravity of 16 samples, then distilled them and determined the amount and the specific gravity of fractions taken every 50° up to 300°.

With the exception of the above, we have been unable to find anything more than a passing allusion to California petroleums. Believing a systematic investigation would prove of value, we have undertaken it with that idea in view.

The oil was furnished us by the Pacific Coast Oil Company and came from Pico Cañon, in the San Fernando mountains, Los Angeles county, at present the most productive field in the State.

The crude petroleum is thick, and dark-green in color, with a specific gravity of 0.8414 at 15° C. and a refractive index of 1.4810 at 14° C. About 18 liters of the crude oil was subjected

[1] Min. Res. of the U. S., Sixth Report. [2] Fourth Ann. Rep. Cal. Min. Bur., p. 295.
[3] Am. Jour. Sci., pp. 43-242.

to fractional distillation, collecting at every ten degrees, each fraction redistilled, collecting at every five degrees, and this repeated for every fraction from three to five times. A very small quantity came over below 40°. When the temperature reached 200° the distillation was conducted under diminished pressure, but the final fractions were obtained under atmospheric pressure, and the temperatures given are at normal pressure. The lower fractions were water-white; the higher, slightly colored and possessed a marked fluorescence. A tendency to collect in larger amounts at 75°–85°, 150°–160°, 190–200° and 240°–250° was observed, but in general the fractions were nearly uniform in amount.

The refractive index and specific gravity of each fraction are given in the following table; the latter was determined with a Westphal balance at a temperature of 15°, the former with an Abbé refractometer.

Boiling-point of Fractions.	Specific Gravity.	Refractive Index.	Boiling-point of Fractions.	Specific Gravity.	Refractive Index.
Below 40°	0.6344	1.3669	180–185	0.8005	1.4451
40–50	0.6545	1.3760	185–190	0.8030	1.4464
50–60	0.6724	1.3846	190–195	0.8062	1.4482
60–65	0.6882	1.3900	195–200	0.8096	1.4500
65–70	0.6996	1.3924	200–205	0.8126	1.4519
70–75	0.7108	1.3982	205–210	0.8153	1.4531
75–80	0.7195	1.4020	210–215	0.8194	1.4553
80–85	0.7278	1.4065	215–220	0.8220	1.4572
85–90	0.7340	1.4090	220–225	0.8268	1.4600
90–95	0.7388	1.4111	225–230	0.8308	1.4621
95–100	0.7433	1.4134	230–235	0.8340	1.4650
100–105	0.7475	1.4165	235–240	0.8391	1.4678
105–110	0.7507	1.4185	240–245	0.8430	1.4699
110–115	0.7533	1.4203	245–250	0.8460	1.4720
115–120	0.7570	1.4222	250–255	0.8498	1.4741
120–125	0.7598	1.4245	255–260	0.8516	1.4760
125–130	0.7635	1.4291	260–265	0.8527	1.4771
130–135	0.7675	1.4301	265–270	0.8549	1.4780
135–140	0.7680	1.4299	270–275	0.8556	1.4787
140–145	0.7719	1.4327	275–280	0.8587	1.4791
150–155	0.7786	1.4344	280–285	0.8595	1.4794
155–160	0.7820	1.4362	285–290	0.8612	1.4795
160–165	0.7855	1.4382	290–295	0.8630	1.4804
165–170	0.7897	1.4404	295–300	0.8649	1.4824
170–175	0.7934	1.4421			
175–180	0.7967	1.4440	Original oil,	0.8414	1.4810

The fractions boiling below 110°, when treated with a mixture of nitric and sulphuric acids until no further action took place, gave a liquid heavier than water, that resembled nitrobenzene in smell and general appearance, but, on attempting to distil it, a sudden decomposition took place. The same thing has been observed in this laboratory in attempting to prepare nitrobenzene from impure benzene; a liquid having the general properties of nitrobenzene is produced, but cannot be distilled without decomposition. A preliminary examination of these fractions shows that the oil contains paraffins, naphthenes, and benzene-homologues, and is apparently intermediate in composition between the Pennsylvanian and Russian petroleums.

A complete chemical investigation of this petroleum is being carried on in this laboratory, and we should therefore like to reserve the field for the present.

CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA.

SOLUBLE PENTOSES IN PLANTS.

BY G. DE CHALMOT.

It has recently been recognised that among the substances occurring most widely distributed in plants are the pentosanes (Tollens),[1] which yield pentoses by hydrolysis and, in many cases, form a considerable part of plants. Tollens and his students found more than 20 per cent. in different kinds of straw, and, later, Flint[2] found as much as 30 per cent. in beech wood and corn stubble.

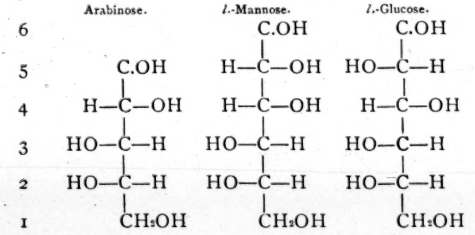
The sugars which have up to the present time been obtained from these pentosanes are arabinose and xylose. The arabinose-carbonic acid obtained by Kiliani[3] by the action of hydrocyanic

[1] Scheibler: Ber. d. chem. Ges. **1**, 58, 108; **6**, 612. R. W. Bauer: J. prakt. Chem. [2] **34**, 47; **43**, 112. Poumarède and Figuier: J. prakt. Chem. [2] **12**, 29. Th. Thompson: Ber. d. chem. Ges. **13**, 2168. F. Koch: Ber. d. chem. Ges. **20**, 145. Tollens, Wheeler, Allen, Günther, DeChalmot: Landw. Vers-Stationen **39**, 401. K. Bicler: Inaug. Diss. (Göttingen, 1890). Stone: Ber. d. chem. Ges. **23**, 3791; **24**, 1657. E. Schulze: Ber. d. chem. Ges. **23**, 3110; **24**, 2270. Winterstein: Ber. d. chem. Ges. **25**, 1237. A. Voswinkel: Pharm. Centrbl. [N. F. VIII] **36**, 505. C. Lintner and G. Dull: Ztschr. angew. Chem. 1891, 538.

[2] Ed. Flint: Inaug. Diss. (Göttingen, 1892).

[3] Ber. d. chem. Ges. **20**, 345.

acid on arabinose was found by Emil Fischer[1] to be identical with *l.*-mannonic acid; and it was also shown that besides the *l.*-mannonic acid some *l.*-gluconic acid was formed in the reaction. The carbon atoms 2 to 4 in arabinose are stereo-isomeric with those in *l.*-mannose and *l.*-glucose, a fact which is best shown by the use of Fischer's formulæ.



Fischer[2] also proved that xylose-carbonic acid is the isomer of *d.*-gluconic acid, which had been obtained by him by the reduction of *d.*-gluco-saccharic acid, and that, therefore, xylose is a laevo compound. All other sugars which have been extracted from plants belong to the dextro series. Now one has either to consider that the plants possess the power of changing dextro sugars into laevo sugars, or that, besides the dextro sugars, laevo sugars are formed by the assimilation-process.

In the first case a decided change would have to take place; but with regard to the second, Emil Fischer[3] and others have referred to the fact that in the artificial formation of compounds with asymmetrical carbon atoms, an equal number of molecules of the dextro and laevo varieties were almost always formed.

He supposed that if in plants we generally found active substances only, it was because the plants had transformed the isomers into some other substances. Baeyer's theory, according to which plants form carbohydrates from formaldehyde, has lately received strong support from two directions. (1) Fischer showed that there were two sugars of the composition $C_6H_{12}O_6$ in the formose prepared by Löw[4] from formaldehyde, and that that one of these which occurred in small quantities only was identical

[1] Ber. d. chem. Ges. **23**, 370 and 2131.
[2] *Ibid.* **23**, 393.
[3] *Ibid.* **23**, 2628; **24**, 528.
[4] J. prakt. Chem. [2] **23**, 321; **34**, 51.

with *i.*-fructose.[1] (2) It was not supposed that the want of carbon dioxide could be supplied to a given plant by formaldehyde until Bokorny[2] recently observed that spirogyra threads in a room free from carbon dioxide grew rapidly in the light at the expense of sodium-oxymethylsulphonic acid, which easily sets free formaldehyde. According to the theory of Baeyer, it seems to me as probable *that plants form pentoses* as that they form hexoses.

I think it is worth the trouble to attempt to find the limit. If pentoses are formed in the leaves of a plant and we find them also in other parts of the plant, it is probable that they have passed to these other parts. The pentosanes so far found form parts of the cell-wall and are soluble in alkalies and in acids only or, in exceptional cases, in boiling water. They correspond to the insoluble hexoses, as cellulose or, perhaps, starch. A migration of this substance as such is not an acceptable explanation, as the pentoses must exist in the plants in an easily soluble form if they really arise by the assimilation-process. In order to prove this I proceeded as follows: 60–80 grams of a finely chopped substance were placed in a 200 cc. wide-neck flask, some drops of chloroform added, the flask filled with distilled water and allowed to stand 12 hours after adding a few more drops of chloroform. The whole mass was then put in a cloth, and the liquid after being pressed out was purified with lead acetate and filtered from the precipitate. It was often necessary to repeat the filtration, as there was further precipitation on standing.

50 cc. of this clear solution was distilled with 50 cc. hydrochloric acid (24 per cent. HCl), and the distillate tested with aniline acetate for furfurol. In this proof I made use of a property possessed by pentoses—that of forming furfurol when heated with hydrochloric acid (12 per cent. HCl).[3] Albuminous bodies which furnish traces of furfurol were not present, but hexoses, which also furnish some furfurol, were always present, and their influence was afterwards shown. Even in solutions which gave much furfurol, the reaction with phloroglucin failed.

I collected the material myself and used the leaves of the following plants in the investigation:

Sonchus asper (Vill.), Compositiae.

Plantago lanceolata (L.), Plantagineae.

[1] Ber. d. chem. Ges. **22**, 359; **23**, 384. [2] Ber. d. bot. Ges. IX, **4**, 103. [3] Tollens: *loc. cit.*

Verbascum Thapsus (L.), Scrophulariaceae.
Bignonia capreolata (L.), Bignoniae.
Solanum Carolinense (L.), Solaneae.
Datura Tatula (L.), Solaneae.
Echium vulgare (L.), Bonaginaceae.
Asclepias Cornutii (Decaisne), Asclepiadaceae.
Forsteronia difformis (A. D. C.)?, Apocynaceae.
Diospyros Virginiana (L.), Ebenaceae.
Vaccinium vacillans (Solander), Ericaceae.
Trifolium pratense (L.), Leguminoseae.
Pirus communis (L.), Rosaceae.
Platanus occidentalis (L.), Platanaceae.
Daucus Carota (L.), Umbellifereae.
Euphorbia corollata (L.), Euphorbiaceae.
Vitis cordifolia (Michx), Vitaceae.
Ailanthus glandulosus (Desf.), Simarubaceae.
Hypericum perforatum (L.), Hypericaceae.
Lepidium Virginicum (L.), Cruciferеae.
Clematis Ochrolenca (Ait.), Ranunculaceae.
Sassafras officinale (Nees), Lauraceae.
Agrostemna Githago (L.), Caryophyllaceae.
Phytolacca decandra (L.), Phytolaccaceae.
Quercus rubra (L.), Cupulifereae.
Quercus prinus (L.), Cupulifereae.
Quercus lyrata (Walt.), Cupulifereae.
Bromus secalinus (L.), Gramineae.
Carere lupulina (Mühl.), Cyperaceae.
Commelina Virginica (L.), Commelinaceae.
Uvularia perfoliata (L.), Liliaceae.
Pinus Taeda (L.), Conifereae.
Aspidium acrostichoides (Schwartz), Filices.

In the distillates collected furfurol could plainly be distinguished, although the reaction was sometimes very weak. The plants which were used belonged to different families, and I do not think that I am making too broad a statement if I assert that *in the leaves of most of the higher green plants a water-soluble substance occurs which forms furfurol.* I have already remarked that it was possible the furfurol was formed from hexoses. In some cases only traces of furfurol were found, and the amount was never very great. In order to prove that the furfurol which was found was

not formed from the hexoses, it was necessary to estimate (1) how much furfurol the hexoses furnished, and (2) how much furfurol and hexoses were present in the solutions used. In order to solve these questions I have devised a method for determining small amounts of furfurol.

Some time ago Stenhouse[1] obtained a dye-stuff from aniline, aniline hydrochloride and furfurol, of the composition $(C_6H_7N)_2$. $C_5H_4O.HCl.H_2O$.

This dye-stuff is always formed if these substances be used; but if there is enough mineral acid present to combine with all the aniline, no color is produced. Acetic acid, however, acts differently, for a red color immediately appears when aniline and furfurol are added to an alcoholic solution of acetic acid, provided the acid is concentrated enough. The color is very intense, and can be observed in very dilute solutions, and is even formed in very dilute solutions of furfurol in acetic acid, a fact which is made use of for the detection of furfurol in the distillates, where the aniline or aniline acetate neutralises the excess of hydrochloric acid.

I made use of this reaction to determine the furfurol present. 1 cc. of a weak solution of furfurol in 5-per cent. acetic acid was treated in a long tube with 1 cc. of a 1-per cent. solution of aniline in 95-per cent. alcohol. The tube was then sealed up, shaken, and placed in the dark. Another tube containing a solution of furfurol (1 part in 10,000) was prepared in the same way, and the two tubes compared after 20 minutes. If the colors were not the same, the stronger was diluted until they were alike. The amount of furfurol in the solutions used was calculated as follows:

A.—If the solution of unknown strength be the stronger,

$$H=\frac{a+2}{2}\times\frac{1}{10000};\text{ but}$$

B.—If the standard solution be the stronger,

$$H=\frac{2}{a+2}\times\frac{1}{10000};$$

where H = value sought, and a = number of cc.'s used. For diluting I always used a mixture of equal parts of the alcoholic aniline solution and of 5-per cent. acetic acid. If I diluted

[1]Ann. Chem. (Liebig) **74**, 282; **156**, 197. Schiff: Ann. Chem. (Liebig) **201**, 355; **239**, 349. De Chalmot: This Journal **14**, 310.

with 50-per cent. alcohol I always added less liquid than the calculated amount, because the aniline acetate formed was somewhat colored, and when a colorless liquid was added this color was diluted too. The acetic acid used was prepared from the sodium salt, for the commercial article often contains traces of furfurol. The alcohol also sometimes contains traces of furfurol which cannot always be removed even by distillation with potassium. To avoid possible mistakes I added a drop of acetic acid to the aniline and allowed it to stand 24 hours before using it, in order to decompose any red coloring matter which was formed at first. This solution had a weak golden-yellow color, which did not interfere with the estimations, if the solutions were diluted as described above. By this method I obtained the following figures:

Calculated.		Found.	
gram furfurol in 1 cc.	cc. necessary to add.[1]	cc. added =	gr. furfurol in 1 cc.
0.001	+ 18	+ 17	0.00095
0.001	+ 18	+ 17.5	0.00097
0.001	+ 18	+ 17.5	0.00097
0.0005	+ 8	+ 8.5	0.000525
0.00004	— 3	— 3	0.00004
0.00004	— 3	— 2.5	0.000044
0.0000167	— 10	— 12	0.000014
0.0000167	— 10	— 9	0.000018
0.0000167	— 10	— 10.5	0.000016

With 0.0000084 gram in 1 cc. no color could be detected. The figures found were sufficient for my purpose. In order to determine the amount of furfurol obtained by the distillation with hydrochloric acid, and to obtain some idea of the yield of furfurol from the materials used, I proceeded as follows:

A weighed amount of leaves was chopped up as fine as possible on a tin plate with a knife and transferred to a flask. After adding a few drops of chloroform, 200 cc. of water and a few more drops of chloroform, and allowing the mixture to stand for 12 hours, 20 cc. of lead acetate were added and enough water to make the volume of the liquid 250 cc. This was then well mixed and, after standing half an hour, brought into a strainer and the liquid pressed out and then filtered. 80 cc. of this solution were put in

[1] The sign + denotes that the unknown solution is the stronger, and — that the standard solution is stronger.

a 100-cc. flask and the excess of lead precipitated with sodium sulphate. The flask was filled up, its contents well mixed and the precipitated lead sulphate filtered off after standing half an hour. 50 cc. of this latter filtrate were distilled with 50 cc. hydrochloric acid (24-per cent. HCl), and the rest used for the determination of the hexoses present (*see below*).

As this solution formed only a small amount of furfurol, only 100 cc. liquid were distilled off. 25 cc. were distilled off slowly with a free flame and then the other 75 cc. more rapidly. 50 cc. of hydrochloric acid (12-per cent. HCl) were added in two portions, the first portion after 25 cc. and the last after 50 cc. had distilled over. The average amount of hydrochloric acid in the distillate was 10 per cent. 16 grams of sodium bicarbonate and 18 grams of sodium acetate were added to this and a solution was obtained, of about 5-per cent. acetic acid and of much sodium chloride and sodium acetate. This was distilled again and the 50 cc. first coming over used in the titration. I afterwards found that the distillate often contained substances which gave a brown color with aniline and interfered with the detection of the red. These substances, however, decompose on standing in the light, while furfurol is not affected, and it was found that without exception the red color could plainly be perceived if the solution was not titrated until the following day.

Even after 24 hours a brown color sometimes remained, and a comparison with a pure furfurol solution was thus not very secure. To test the method the following analyses were made:

1 cc. of 1-per cent. furfurol solution, 100 cc. of 5-per cent. acetic acid, 17 grams sodium chloride and 7 grams sodium acetate were distilled, and 50 cc. were collected.

	Calculated.	Found. I.	II.
Furfurol=	+2 cc.	+2 cc.	+(1.5–2) cc.
1 cc. of the solution=	0.0002	0.0002	0.00019 gram

Bignonia capreolata (L.).

I. 80 grams in 250 cc. Furfurol=+7.5 cc. 1 cc. of the solution=0.000475 gram of furfurol.

II. 80 grams in 250 cc. Furfurol=+8 cc. 1 cc. of the solution=0.0005 gram of furfurol.

I. 80 grams in 250 cc. Furfurol=+7.5 cc. 1 cc. of the solution=0.000475 gram of furfurol.

II. 40 grams in 250 cc. Furfurol = + 2.75 cc. 1 cc. of the solution = 0.00024 gram of furfurol. Calculated according to I, it is 0.00024 gram of furfurol.

III. 20 grams in 250 cc. Furfurol = + 0.75 cc. 1 cc. of the solution = 0.00014 gram of furfurol. Calculated according to I, it is 0.00012 gram of furfurol.

Vitis cordifolia (Michx).

I. 80 grams in 250 cc. Furfurol = — 0.75 cc. 1 cc. of the solution = 0.000073 gram of furfurol.

II. 80 grams in 250 cc. Furfurol = — 0.5 cc. 1 cc. of the solution = 0.00008 gram of furfurol.

III. 30 grams in 250 cc. Furfurol = — 10 cc. 1 cc. of the solution = 0.000016 gram of the furfurol. Calculated according to II, it is 0.00003 gram of furfurol.

By this method it was possible for me to answer the question, whether furfurol, which is formed by the distillation of the solution with hydrochloric acid, could or could not be formed from hexoses. I determined the amount of furfurol which soluble hexoses could form, by cane sugar. Commercial granulated sugar was recrystallised from dilute alcohol.

I. 0.1 gram of cane sugar gave traces of furfurol which, however, were only apparent when several cc. were used. By the titration-method no color could be perceived. 1 cc. therefore contained less than 0.000008 gram of furfurol, and 0.1 gram of cane sugar gave less than 0.0004 gram of furfurol.

II. 0.1 gram of cane sugar gave traces of furfurol and no color by titration. Contained less than 0.0004 gram of furfurol.

III. 0.5 gram of cane sugar; slight color visible. 1 cc. contained between 0.00002 and 0.000008 gram of furfurol, or 0.5 gram of cane sugar formed 0.001–0.0004 gram of furfurol.

IV. 0.5 gram cane sugar; result same as III.

Therefore 1 gram of invert sugar (=0.95 gram cane sugar) gave, at the most, 0.0019 gram of furfurol, or about 0.2 per cent.

I now took some of the leaves which, in my opinion, yielded the smallest amount of furfurol and estimated in the solution the furfurol and hexoses. I could make only an approximate determination of the largest amount of hexoses possible. 40 cc. of the clear solution (see above) were treated successively with lead acetate and with sodium sulphate, and after being subjected to the

process of inversion and neutralised, were filled up to 50 cc. The traces of dissolved chloroform, which would even reduce copper, were removed by inversion.

Fehling's solution was titrated with the liquid thus obtained. I titrated only 2 cc. of the Fehling's solution (1 cc. of blue and 1 cc. of white), which I diluted to 50 cc. The value of the Fehling's solution[1] was estimated by 0.25-per cent. invert sugar solution made according to Soxhlet:[2]

2 cc. of the Fehling's solution was reduced by 4.5 cc. of this solution and was equivalent to 0.01125 gram of invert sugar.

Trifolium pratense (L.).

Used 70 grams; 2 cc. Fehling's solution = 7 cc. of the solution; furfurol = + 2.5 cc.

1 gram substance = 0.0089 gram of invert sugar.[3]

1 gram substance = 0.001 gram of furfurol.

The amount of hexoses present in 1 gram of the substance could have furnished, at the most, 0.0000178 gram of furfurol.

Solanum Carolinense (L.).

Used 70 grams; 2 cc. Fehling's solution = 18.2 cc. of the solution; furfurol = — (1.5–2) cc.

1 gram substance = 0.0035 gram of invert sugar.

1 gram substance = 0.00023 gram of furfurol.

The hexoses could have formed, at the most, 0.000007 gram of furfurol.

Verbascum Thapsus (L.).

Used 80 grams; 2 cc. Fehling's solution = 4 cc. of the solution; furfurol = — 8.5 cc.

1 gram substance = 0.0136 gram of invert sugar.

1 gram substance = 0.000084 gram of furfurol.

The hexoses could have formed, at the most, 0.000027 gram of furfurol.

Trachelospermum difforme (Gray ?).

Used 80 grams; 2 cc. Fehling's solution = 3 cc. of the solution; furfurol = —3 cc.

[1] The copper sulphate used was somewhat weathered.

[2] J. prakt. Chem. [2] **21**, 228.

[3] These figures are too high, as I took no account of the solid matter and air in the solution; but the figures for the furfurol and invert sugar are subject to the same errors.

1 gram of the substance = 0.0183 gram of invert sugar.

1 gram of the substance = 0.00016 gram of furfurol.

The hexoses could have formed, at the most, 0.000037 gram of furfurol.

Daucus Carota (L.).

Used 80 grams; 2 cc. Fehling's solution = 3 cc. of the solution; furfurol = —1.5 cc.

1 gram of the substance = 0.0183 gram of invert sugar.

1 gram of the substance = 0.00022 gram of furfurol.

The hexoses could have formed, at the most, 0.000037 gram of furfurol.

From the figures obtained it appears that in all the cases examined the amount of hexoses was not sufficient to explain the formation of furfurol.

As I have already stated, the five plants used in this investigation are those which in my opinion were shown, in the first investigation, to yield the smallest amount of furfurol, and with the exception of *Trifolium*, this suggestion seems to be true.

I extend my previous conclusion and now express it as follows:

In most (all) of the higher green plants there are soluble substances in the leaves which form furfurol, and are neither albuminous substances nor hexoses, but must be regarded in the present state of our knowledge as pentoses.

The amount of soluble pentoses in the leaves is very small and much less than that of the hexoses.

While I considered that these soluble pentoses furnish 50 per cent. of the furfurol, I calculated the following approximate figures:

	Hexose.	Pentose.
Bignonia	...	0.37 per cent.
Trifolium	0.89 per cent.	0.20
Solanum	0.35	0.45
Daucus	1.80	0.45
Trachelospermum	1.80	0.03
Verbascum	1.40	0.008

The investigations described were carried on with leaves, and it is possible that a soluble pentose might be present in these which was absent in the rest of the plant and therefore did not serve as a carrier of the pentose. For this reason I examined the bark also, and in this investigation used only the colorless bark of young limbs.

Ailanthus glandulosus (Desf.).

Used 80 grams; furfurol = —1.5 cc.; 1 gram substance = 0.00022 gram of furfurol.

Sassafras officinale (Nees).

Used 80 grams; 2 cc. Fehling's solution = 2.5 cc. of the solution; furfurol = —(1.5–2) cc. 1 gram substance = 0.022 gram of invert sugar; 1 gram substance = 0.00021 gram of furfurol. The hexoses could have formed, at the most, 0.000044 gram of furfurol.

Quercus rubra (L.).[1]

Used 80 grams; 2 cc. Fehling's solution = 5.5 cc. of the solution; furfurol = —0.5 cc. 1 gram substance = 0.01 gram of invert sugar; 1 gram of substance = 0.00031 gram of furfurol. The hexoses could have formed, at the most, 0.00002 gram of furfurol.

According to this, *soluble pentoses occur in the colorless bark of higher green plants.* If the soluble pentoses found were transportable substances, it seems to me likely that they would easily diffuse through membranes permeable to water. It was shown that large quantities of the substances in the sap of the *Phytolacca* which form furfurol, could diffuse through parchment paper in 36 hours.

Further experiments were conducted as follows:

Datura Tatula (L.).

200 cc. of the pressed-out sap were treated successively with lead acetate and with sodium sulphate, and the clear liquid placed in a dialyser of parchment with distilled water outside. The analysis of the liquid outside, after 6 hours, was as follows: 2 cc. of Fehling's solution = 7.5 cc. of the solution (in which the process of inversion had taken place; furfurol = —(1.5–2) cc. 1 cc. = 0.0019 gram of invert sugar; 1 cc. = 0.000053 gram of furfurol. The hexoses could have formed, at the most, only 0.0000038 gram of furfurol.

Phytolacca decandra (L.).

The conditions were the same in this case as in the last, and the results were as follows:

[1] Part of the young wood was still adhering to the bark.

2 cc. of Fehling's solution = 17 cc. of the solution (also changed by inversion); furfurol = —1.5 cc. 1 cc. = 0.0008 gram of invert sugar; 1 cc. = 0.000057 gram of furfurol. The hexoses could have formed, at the most, 0.0000016 gram of furfurol.

By this it is proved that *the soluble pentoses are easily diffusible.* The question arises now, whether we shall regard them as simple sugars or as more complex substances. The solubility and diffusibility point towards the former. Moreover, the complex pentoses generally have an acid character, so, had soluble salts been present, they would probably have been precipitated by the lead acetate. I think, therefore, *that there are present in plants simple pentoses which serve as transporting substances.* Absolute proof of this could be obtained if the sugar could be isolated; and this seems to be not at all impossible—for instance, from the leaves of the *Bignonia*, in which I calculated there was about 0.4 per cent. Most of the hexoses can be easily separated from a solution by fermentation; but I could not carry out this line of investigation, as my laboratory was not fitted up for such work. It seemed probable that *the small amount of soluble pentoses would be scarcely diminished upon the death of the leaves*, if these substances were only migratory substances; and such proved to be the case, as the plants used lost their leaves about the beginning of September from a drought.

Pirus communis (L.).

From this tree I collected equal numbers of green and of yellow leaves of the same size. The yellow leaves were about to fall.

I. August 26.

Yellow.	Green.
112 leaves weighing 26 grams:	112 leaves weighing 31 grams:
Furfurol = —0. cc.	Furfurol = —(0.5–1.) cc.

The aniline reaction of the yellow leaves upon the addition of 0.5 cc. was the same as that of the green. The proportion of soluble pentoses in the yellow leaves to those in the green was about as 5 : 4.

II. August 29. (The same tree.)

Yellow.	Green.
128 leaves weighing 27.5 grams:	128 leaves weighing 32.5 grams:
Furfurol = ±0. cc.	Furfurol = —0.5 cc.

The aniline reaction and the proportion were the same here as in the last case.

Bignonia capreolata (L.).

Yellow and green leaves of the same size were used.

Yellow. Green.

500 leaves weighing 60.5 grams: 500 leaves weighing 70.5 grams: Furfurol = +3.5 cc. Furfurol = +5. cc.

0.5 cc. had to be added to the green leaves in order to make the two agree by the aniline reaction. The proportion of soluble pentoses in yellow and green leaves was as 4 : 5.

If by the assimilation-process pentoses are formed, it is probable that they cannot pass out of the leaves as fast as they are formed. The hexoses, as is well known, are deposited as starch. I shall return to the question whether or not pentoses too are deposited temporarily as solid matter. I shall now point out that most probably there are more soluble pentoses in the leaves in the evening than in the morning, assuming that the theory of their formation by assimilation is correct.

If the pentoses are temporarily precipitated after their formation by the assimilation-process, then, presumably, they migrate after the principal assimilation is over. If the pentoses accumulate only in solution, the difference between the various parts of the plants might be equalised by the next morning. In the first case the difference in the amount of soluble pentoses in the leaves in the morning and in the evening would be less striking than in the latter. I thought it would repay one to examine this.

An investigation was first carried on with *Bignonia capreolata*, which contains a large amount of soluble pentoses. I collected the samples carefully and made four determinations of each, but found no great difference between the leaves collected in the morning and those in the afternoon. *Platanus* gave no results, although three experiments were made with material from different stations. *Quercus* gave different results, which I shall give here.

Quercus Lyrata (Walt.).

1. Damp ground. Leaves from a small tree which had a southern exposure. A sunny day.

August 11, 8.30 P. M.; 30 leaves = 535 × 305.5 cm.; 2 leaves = 31 × 17; 32 = 566 × 325.5 cm. Furfurol = —(3–4) cc.

August 12, 4.30 A. M.; 30 leaves = 564 × 321.5 cm. = 48.5 grams. Furfurol = —11 cc.

The reaction was much stronger in the evening, than in the morning leaves.

2. Same place and conditions.

August 19, 7 P. M.; 50 leaves = 702 × 393.5 cm. = 43.5 grams. Furfurol = —1 cc.

August 19, 4.30 A. M.; 50 leaves = 703.5 × 393 cm. = 43.5 grams. Furfurol = —(1.5–2) cc.

The leaves collected in the evening were 0.5–1 cc. stronger than those gathered in the morning.

3. Damp ground, southern exposure. Specimen was taken from a tree. The day was slightly cloudy.

August 22, 9 P. M.; 46 leaves = 629 × 277.5 cm. = 34 grams. Furfurol = —2.5 cc.

August 22, 4.30 A. M.; 46 leaves = 651.5 × 243.5 cm. = 39.5 grams. Furfurol = —1 cc.

The leaves in the evening were 0.5–1 cc. weaker than in the morning.

4. Same plant as those used in 3. Dark day.

August 24, 8.30 P. M.; 45 leaves = 620 × 318 cm. = 35.5 grams. Furfurol = —2 cc.

August 24, 4.30 A. M.; 45 leaves = 619 × 314 cm. = 35.5 grams. Furfurol = —(2.5–3.) cc.

Leaves gathered in evening were 0.5 cc. stronger than those gathered in morning.

5. In the valley. A bush. A partly cloudy day.

August 29, 8 P. M.; 30 leaves = 513 × 248.5 cm. = 37.5 grams. Furfurol = —1 cc.

August 30, 4 A. M.; 30 leaves = 513.5 × 248 cm. = 36.5 grams. Furfurol = —1.5 cc.

Leaves gathered in the evening were 0–0.5 cc. stronger than those gathered in the morning; this difference is quite perceptible.

6. Large tree near the bush used in 5; all the leaves from the same branch.

August 29, 8 P. M.; 49 leaves = 651 × 379 cm. = 45 grams. Furfurol = —(0.0–0.5) cc.

August 30, 4 A. M.; 49 leaves = 649 × 381.5 cm. = 45 grams. Furfurol = —1 cc.

Leaves gathered in evening were 0.5 cc. stronger than those gathered in the morning.

Quercus prinus (L.).

7. A tree on a southern exposure. Sunny day.

August 15, 8.30 P. M.; 45 leaves 661.5 × 313 cm. = 51.5 grams. Furfurol = ± 0 cc.

August 15, 4.30 A. M.; 45 leaves = 664 × 314 cm. = 57 grams. Furfurol = —2 cc.

Leaves gathered in the evening were 1.5–2 cc. stronger than those gathered in the morning.

8. August 16, 7.30 P. M.; 45 leaves = 668 × 314 cm. = 48 grams. Furfurol = —1 cc.

August 16, 5 A. M.; 45 leaves = 657 × 313.5 cm. = 49.5 grams. Furfurol = —2.5 cc.

Leaves gathered in the evening were 0.5–1 cc. stronger than those gathered in the morning.

Quercus rubra (L.).

9. August 24, 8 P. M.; 25 leaves = 450 × 280 cm. = 49.5 grams. Furfurol = —(2–2.5) cc.

August 24, 5.30 A. M.; 25 leaves = 451 × 279 cm. = 48 grams. Furfurol = —2 cc.

Leaves gathered in the morning same as those gathered in the evening.

In comparing these results one cannot help concluding that they agree very closely, especially when he recognises that the methods of research were not very exact, and that the samples were collected altogether in the woods, which makes it quite difficult to obtain accurate samples.

In these experiments in seven cases there was unquestionably an excess of soluble pentoses in the leaves gathered in the evening over that in those gathered in the morning. In one case (*Quercus rubra*) the amount was about the same in both sets of leaves. In experiment 3, the leaves gathered in the morning were richer; but in experiment 4, the leaves of the same plant were used and the result was reversed.

I would be justified in concluding from this that *in the leaves of* Quercus (lyrata *and* prinus) *there are more soluble pentoses present in the evening than in the morning.* I carried out no investigations with other plants, the difficulty of gathering samples in the woods being considerable, especially at night; nevertheless I hope to repeat these experiments and to extend them. I was not surprised that species of oak acted as described, since the wood of the nearly related beech contains a very large amount of

pentosanes. I did not obtain any positive knowledge as to the amount of pentosanes in oak wood, but I found that C. Koch had extracted 10 per cent. of gum from it and that this probably contained only a small part of the pentosanes present.

I return now to the hypothesis which was mentioned above: *Pentoses which arise by assimilation-processes should, like the hexoses, be precipitated in changing to an insoluble form.* If pentoses and hexoses are formed at the same time, it would be necessary for me to accept this hypothesis. I suppose it would be necessary, in order that the assimilation might be continuous, that the parts assimilated should be removed or precipitated to give an opportunity for continued action. It might not be possible for the plants to convey them away as fast as they are formed, in which case they would be precipitated. One must assume a temporary precipitation of the pentoses in the chlorophyl grains mixed with the hexoses as parts of the starch of assimilation. Unfortunately there is no means available at present for identifying a pentose under the microscope, although it may soon be possible. The presence in plants of pentosanes which act very much like starch is very probable, since Winterstein[1] obtained 15 per cent. of furfurol from the amyloid materials of the poconia and balsam seeds.

Although there are more soluble pentoses in the oak leaves in the evening than in the morning, still the difference is only slight. It was impossible for me to detect any difference using *Bignonia* and *Platanus* leaves. It does not seem to me possible that the excess of the soluble pentoses found in the oak makes up the whole or any considerable part of the pentoses assimilated daily. It is very probable that the principal migration of the pentoses stored up during the daytime commences at sunset, just as this is believed of the hexoses. I have carried on experiments to determine whether or not a difference in the amount of pentoses in the leaves in the morning and at night can be proved. In the leaves of the trees which were most suitable for the purpose I found about 10 per cent. of the dry substance was pentosanes. If only a small part of this be carried away during the night it would be very difficult to detect it, and very exact methods would have to be used to determine it. The experiments which have been carried on later suggest that more pentosane is present in the evening, but the results are not sufficient even for a pre-

[1] See ref. 1.

liminary statement. I hope to continue this work next summer and carry the investigations further. Let it be understood, however, that I am not inclined to regard the hypothesis offered as entirely true, for I fear I have gone too far in my attempts to find an analogy with the hexoses; but if the hypothesis is proved, it and the results communicated above will safely establish the origin of pentoses by assimilation. I must finally return to my former proposition that the substance assimilated should be withdrawn from further action in order that there may be continued assimilation.

I do not propose to suggest any new hypothesis; on the contrary I think it highly probable that this has already been pointed out, but I do not know that such is the case. It will, however, do no harm to make some remarks on the subject.

Although in the plants other carbohydrates than pentoses are present, perhaps nonose (Fischer) and others, yet the greater part of the dried material consists of hexoses and hexosanes. The starch formed by assimilation behaves micro-chemically like that formed in other ways, and probably consists of hexosanes. The conception that plants form chiefly hexoses by assimilation is still universal.

By the same reactions one can make heptose artificially from hexose, octose from heptose, etc., just as well as hexose from pentose. If plants really form hexoses by condensation from simpler aldehydes, there is no apparent reason why the condensation should not go further and why larger amounts of heptoses, octoses, nonoses, etc., should not be formed. Fischer[1] thinks that plants form hexoses and, perhaps, nonoses from glyceric aldehyde, but the nonoses have not been isolated, as their behavior is very similar to that of the glucoses. This is, however, only a supposition which does not explain the formation of pentoses. Under the conditions in which a condensation of $x CH_2O$ to $(CH_2O)_x$ takes place in the plants, the reverse might also be possible; we ought then to express the equivalent reaction thus:

$$x(CH_2O)_n \gtrless (CH_2O)_{x \times n}.$$

This seems possible especially as there is here simple condensation only, without any closing of rings. The compounds $x CH_2O$ in which $x < 5$, ought then to be present, but they have not yet been isolated from the higher plants. By the

[1] Ber. d. chem. Ges. **23**, 2238.

artificial condensation of formic aldehyde a mixture of compounds in different stages of the condensation was actually obtained. If the substances formed in some special stage of the reaction are removed or precipitated, the preceding statements become clear.

Résumé.

There are generally present in plants substances (pentosanes) which form pentoses.

All the natural pentoses so far known belong to the *l.*-series, and all the natural hexoses to the *d.*-series. Plants by assimilation either form hexoses and pentoses, or have the power to change *d.*- into *l.*-compounds. The theory of Baeyer, which has lately received fresh support, makes it not improbable that both hexoses and pentoses are formed. The present work was undertaken to determine the limits of the reactions. Soluble pentoses which could be identified as wandering substances were sought.

It was possible in all the cases which were examined to show the presence of soluble substances which form furfurol; but these substances might be hexoses which furnish traces of furfurol. On this account it was necessary to estimate how much furfurol the hexoses which were present could form and how much furfurol was formed.

For the estimation of small amounts of furfurol a method was devised which depended on the color-reaction between furfurol and aniline in acetic-acid solution.

By this method it was proved that the amount of hexoses present was not at all sufficient to explain the formation of all the furfurol, and that therefore soluble pentoses were present.

For these experiments leaves and colorless bark were used. The amount of soluble pentoses is much less than that of soluble hexoses.

The soluble pentoses are easily diffusible through membranes. The facts lead to the conclusion that the soluble pentoses are simple sugars, $C_5H_{10}O_5$. The investigation confirmed the belief that the small amount of soluble pentoses is not perceptibly diminished by the death of the leaves. In the leaves of the oak there was found in the evening a small but evident excess in the amount of soluble pentoses over that found in the morning. Joined to this is the hypothesis that the pentoses are temporarily converted into stable forms directly after their formation by the assimilation-process. This hypothesis will be further discussed.

Contribution from the Chemical Laboratory of Clark University.

METAMIDOPHENOL AND ITS DERIVATIVES.

First Paper.

By M. Ikuta.

By the reduction of metanitrophenol (melting-point, 96°) with tin and hydrochloric acid, Bantlin[1] obtained a hydrochloride of a base crystallising in colorless grains, which is stable only in the dry state. On account of its instability, the free base could not be isolated. The same salt seems to have been obtained later by Pfaff[2] as a reduction-product of monobrommetanitrophenol of the melting-point 110°. The free metamidophenol being considered to be very unstable, only few of its derivatives,—namely, the methyl[3] and ethyl[4] ethers—have been obtained from the corresponding ethers of metanitrophenol by reduction.

Since the discovery of excellent dyestuffs of the rhodamine group[5] in 1887, metamidophenol and its alkyl derivatives have attained such an importance in the color industry that a number of new methods[6] for producing the same have been patented. According to these patents, metamidophenol is a crystalline body remarkably stable in the air. As the latter methods afford us a ready means of obtaining the substance, it seemed desirable to investigate and characterise it from a scientific side, and to confirm the one or the other statement, which are in themselves widely different.

The result of my work, which will be continued and extended to mono- and dialkyl derivatives, confirms the latter statement—namely, that metamidophenol is a remarkably stable and crystalline body, forming a number of well defined derivatives.

Metamidophenol, $C_6H_4{<}^{OH\ (1)}_{NH_2\ (3)}$.—The substance is made according to the method of A. Leonhardt & Co.,[7] which not only

[1] Ber. d. chem. Ges. **11**, 2101. [2] *Ibid.* **16**, 613.
[3] Pfaff: *Ibid.* **16**, 614, 1139. [4] Wagner: J. prakt. Chem. [2], **32**, 73.
[5] D. R. P. (German patent) 44005, Badische Anilin und Soda Fabrik.
[6] D. R. P. 44792, Bad. A. & S. F.; D. R. P. 48151, Bad. A. & S. F.; D. R. P. 49060, A. Leonhardt & Co.
[7] D. R. P. 49060.

gives a fair yield, but is simple in operation and best adapted for laboratory preparation:

A mixture of 10 grams resorcin, 6 grams ammonium chloride and 20 grams ammonia (10-per cent.), is heated in a sealed tube at 200° for ten hours. The resulting pale-yellow solution is acidified with a large excess of hydrochloric or sulphuric acid, and extracted with ether to free it from unchanged resorcin. On neutralising with soda, part of the metamidophenol separates out in greenish-gray crystals. Ether extracts the rest of the substance from the mother-liquor. It is best purified by dissolving the crude product in toluene, in which the coloring impurities are not soluble, while the substance crystallises out almost immediately in colorless prisms, having a constant melting-point of 122°–123°. D. R. P. 44792 gives the melting-point as 121° and D. R. P. 49060 as 120°. About 50 per cent. of the theoretical yield is thus obtained pure.

For the analysis, it was recrystallised from benzene and dried at 100°.

0.1511 gram substance gave 0.3650 gram CO_2 and 0.0924 gram H_2O.

0.2001 gram substance gave 24.2 cc. N at 30° and 751 mm.

	Theory for C_6H_7NO.	Found.
C	66.05	65.88
H	6.42	6.79
N	12.84	12.96

The substance is easily soluble in alcohol, ether, glacial acetic acid, and water; less soluble in toluene and benzene; and practically insoluble in chloroform, carbon bisulphide and petroleum ether. It is freely soluble in acids and alkalies, forming crystalline salts with the former.

Its alkaline solution is not stable in the air, and even its aqueous solution is very sensitive towards all oxidising agents, including ferric chloride, which gives a brownish-yellow color.

With benzoquinone, it forms a dark-violet body, crystallising in scales.

Metamidophenol, when pure and dry, can be kept without change.

Salts of metamidophenol.—Hydrochloric, hydrobromic, hydriodic and sulphuric acids form with metamidophenol very stable

and crystalline salts. These are extremely soluble in water, but are not deliquescent; they are more or less easily soluble in boiling absolute alcohol. They can be sublimed with partial decomposition. The aqueous solutions are strongly acid towards litmus.

All the salts described below were made by adding a calculated quantity of metamidophenol to the respective acids (1 molecule) and evaporating on a water-bath until crystals begin to appear on the surface. While the solution was slowly cooling in a desiccator, most of the salt separated out in large transparent crystals. After drying on clay plates, it was again recrystallised from water.

The hydrochloride, $C_6H_7NO.HCl$, crystallises in colorless prisms from water and melts at 229°.

0.2014 gram substance, dried at 110°, gave 0.1983 gram AgCl.

	Theory for $C_6H_7NO.HCl$.	Found.
Cl	24.39	24.35

The hydrobromide, $C_6H_7NO.HBr$, crystallises in colorless prisms and melts at 224°.

0.1995 gram substance, dried at 110°, gave 0.1963 gram AgBr.

	Theory for $C_6H_7NO.HBr$.	Found.
Br	42.11	41.87

The hydriodide, $C_6H_7NO.HI$, crystallises in similar prisms and melts at 209°.

0.2001 gram substance, dried at 110°, gave 0.1982 gram AgI.

	Theory for $C_6H_7NO.HI$.	Found.
I	53.48	53.43

The acid sulphate, $C_6H_7NO.H_2SO_4$, crystallises in colorless, rectangular tablets or in needles, and melts at 152°.

0.2056 gram substance, dried at 105°, gave 0.2341 gram $BaSO_4$.

	Theory for $C_6H_7NO.H_2SO_4$.	Found.
H_2SO_4	47.34	47.87

Monacetylmetamidophenol (*metoxyacetanilide*), $C_6H_4<^{OH}_{N=C_2H_4O}$.—1 gram metamidophenol mixed with 1.1 grams acetic anhydride warms up immediately to form a clear solution. In a few minutes the whole thing solidifies to a crystalline mass, consisting of fine needles. After digesting with a little water and filtering, the product is practically pure. It may be

further purified by recrystallisation from water and is thus obtained in colorless needles, melting at 148° to 149°.

0.1540 gram substance, dried at 105°, gave 0.3574 gram CO_2 and 0.0859 gram H_2O.

0.1979 gram substance, dried at 105°, gave 17 cc. N at 30° and 753 mm.

	Theory for $C_8H_9NO_2$.	Found.
C	63.57	63.29
H	5.96	6.19
N	9.27	9.23

It is easily soluble in alcohol and in water, and difficultly soluble in benzene, ether, and chloroform. On account of its greater solubility in water than in ether, the presence of a free hydroxyl group is recognised by using a cold saturated solution containing undissolved substance, which is immediately dissolved on adding a few drops of sodic hydrate.

It gives no isocyanide reaction with chloroform and alcoholic potash, and forms a benzoyl derivative by means of Baumann-Schotten's reaction.

Diacetylmetamidophenol, $C_6H_4<\begin{matrix}O.C_2H_3O\\N=C_2H_4O\end{matrix}$.—1 gram metamidophenol is mixed with 3 to 4 grams of acetic anhydride. In order to complete the reaction, the mixture is heated up to about 150° to 160° for from two to three hours. The product is digested with absolute alcohol and evaporated on a water-bath. The thick oily residue is then taken up with ether, and the latter is repeatedly washed with dilute sodic hydrate and sulphuric acid. After drying the ethereal solution with calcium chloride and evaporating off the ether, 1.5 grams of colorless oil are left behind. The oil will solidify on standing for several hours. It is purified by dissolving in benzene to which a little petroleum ether is added afterwards. Diacetylmetamidophenol will crystallise out in colorless scales, melting constant at 101°.

0.2014 gram substance, dried at 75°, gave 0.4575 gram CO_2 and 0.1103 gram H_2O.

0.1659 gram substance, dried at 75°, gave 11 cc. N at 27° and 750 mm.

	Theory for $C_{10}H_{11}NO_3$.	Found.
C	62.17	61.95
H	5.69	6.03
N	7.25	7.22

The substance is easily soluble in alcohol and ether, less so in benzene and water, and but very slightly soluble in petroleum ether. Its solution in water is unaffected by ferric chloride.

Dilute acids and alkalies do not extract the substance from its ethereal solution.

Monobenzoylmetamidophenol (*metoxybenzanilide*), $C_6H_4<^{OH}_{N=C_7H_6O}$.—1 gram of the dibenzoylmetamidophenol described below is dissolved in absolute alcohol and to the solution the theoretical amount of alcoholic potash (2 molecules) is added. The mixture is kept boiling on a water-bath for about two hours. Potassium benzoate will separate out in colorless scales; this is filtered off and the filtrate is evaporated to dryness. The residue is dissolved in about 10 cc. of water containing a little sodic hydrate. Dilute acid will then precipitate the substance in the form of a white powder. After crystallising twice from toluene, it is obtained in colorless silky needles melting at 174°.

0.1479 gram substance, dried at 125°, gave 0.3967 gram CO_2 and 0.0722 gram H_2O.

0.2281 gram substance, dried at 125°, gave 13.7 cc. N at 30° and 751 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	73.15
H	5.16	5.42
N	6.57	6.44

The substance is very easily soluble in alcohol and in ether; less so in toluene and in chloroform, and sparingly soluble in benzene and water. Sodic hydrate dissolves the substance without change.

The isomeric benzoyl derivative $NH_2.C_6H_4.O.C_7H_5O$ could not be obtained from the dibenzoyl body by saponification with either acid or alkali.

Dibenzoylmetamidophenol, $C_6H_4<^{O.C_7H_5O}_{N=C_7H_6O}$. — 1.5 grams metamidophenol, dissolved in 15 grams sodic hydrate (10-per cent.), and 4 grams benzoyl chloride are gradually mixed together with brisk shaking. A thick oil is at first formed, but it solidifies to a hard crust on standing. The crude product is powdered in a mortar and washed thoroughly with a fresh quantity of sodic

hydrate. On crystallising twice from benzene, the substance is obtained in minute bundles of prismatic crystals. It can be recrystallised from absolute alcohol, from which it separates out in colorless scales. The melting-point is 153°.

0.2041 gram substance, dried at 125°, gave 0.5660 gram CO_2 and 0.0978 gram H_2O.

0.2479 gram substance, dried at 125°, gave 10.5 cc. N at 27° and 748 mm.

	Theory for $C_{20}H_{18}NO_3$.	Found.
C	75.71	75 63
H	4.73	5.32
N	4.42	4.59

It is moderately soluble in alcohol and in chloroform; less so in benzene; sparingly soluble in ether, and insoluble in water and in petroleum ether. The substance is insoluble in dilute acids and alkalies.

Tribrommetamidophenol, $C_6HBr_3<^{OH}_{NH_2}$.—1 gram metamidophenol, dissolved in glacial acetic acid (95-per cent.), is treated with 4.5 grams of bromine. The latter is readily absorbed with a separation of a white precipitate, hydrobromic acid being at the same time evolved. Water is then added, when a large quantity of bulky white needles is thrown down. After drying on a clay plate, the product is purified by dissolving it in petroleum ether, (boiling-point 70°–80°), from which it crystallises out in bright long needles melting at 121°.

0.2319 gram substance, dried at 100°, gave 8 cc. N at 22° and 763 mm.

0.1582 gram substance, dried at 100°, gave 0.2560 gram AgBr (Carius).

	Theory for $C_6H_4Br_3NO$.	Found.
N	4.04	3.92
Br	69.36	68.52

Tribrommetamidophenol is easily soluble in alcohol and in acetic acid; less so in petroleum ether, and slightly soluble in boiling water with decomposition.

It is freely soluble in dilute alkalies, but on account of its negative groups, the substance is no longer soluble in acids.

WORCESTER, MASS., *August,* 1892.

THE SOLUBILITY OF TRIPHENYLMETHANE IN BENZENE.

By C. E. Linebarger.

There is undoubtedly an intimate relation between the surface energy of crystals and their power of entering into solution. The "solution-tensions" of the various forms in which the same chemical substance can crystallise are different; their solubilities accordingly differ, for saturated solutions are cases of dynamical equilibrium, *i. e.* the velocity with which molecules detach themselves from the solid to enter into solution becomes equal to the velocity with which molecules are precipitated from solution upon the solid. The nearer study of the crystalline forms of compounds, especially organic, shows that they are numerous and varied. Triphenylmethane, for instance, exhibits a great variety of crystals, which have been studied by Nölting.[1] It was my intention in beginning this investigation to determine the solubility of some of the polymorphic forms described by him. I found, however, that their solubilities are so nearly identical and the labile modifications pass so easily into the stable, that it was impossible to obtain results that might be counted as reliable for all forms. In this paper there are given only the solubility of the molecular compound of triphenylmethane and benzene, $(C_6H_5)_3CH + C_6H_6$, and that of the stablest form of triphenylmethane (obtained by slow crystallisation from alcohol) in benzene.

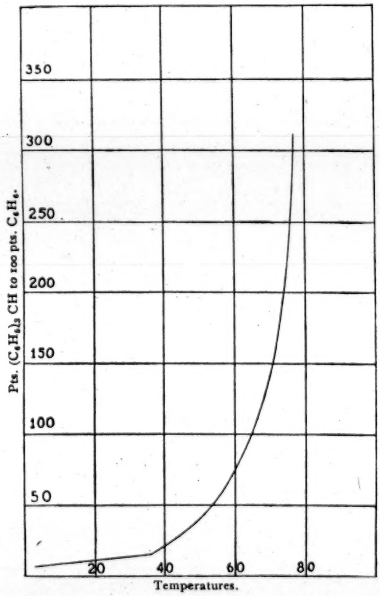
The determinations were made as follows: The solid compound in large excess was for two to three hours shaken up frequently with benzene in a flask set in a thermostat, the temperature of which did not vary more than 0.1° during the determination. A portion of the solution was then pipetted off into a small long-necked flask and, after weighing, the benzene distilled off by means of a free flame. To remove the last traces of benzene from the residual triphenylmethane, the flask was set in an air-bath kept at a temperature of 200°. About 20 grams of solution were taken for each determination, and duplicates did not vary more than one or two figures in the second decimal place. The results are given in Table I and represented graphically in Fig. 1.

[1] Ztschr. Kryst. **5**, 472.

TABLE I.

Temperatures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.	Temperatures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.	Temperatures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.
3.9°	3.90	19.4°	7.24	50.1°	30.64
4	4.06	23.1	8.95	55.5	40.51
12.5	5.18	37.5	10.48	71.	140.00
13	5.51	42.	19.61	76.2	319.67
16.1	6.83	44.6	22.64		

FIG. 1.



If a solution of triphenylmethane in benzene be cooled slowly, supersaturation being prevented by the addition of crystals of triphenylmethane and benzene, the molecular compound of the two hydrocarbons, $(C_6H_5)_3CH + C_6H_6$, crystallises out until the temperature 3.9° is reached. At this point crystals of benzene begin to form also. The curve of solubility here meets the curve

which expresses the dependence of the freezing-point of the solution upon its concentration. As the benzene freezes, the concentration of the solution becomes greater and a corresponding quantity of the double compound, $(C_6H_5)_3CH + C_6H_6$, separates out. A mechanical mixture of crystallised benzene and the double compound, $(C_6H_5)_3CH + C_6H_6$, in proportions corresponding to the concentration of the saturated solution is accordingly obtained. As such a solution does not become changed through partial solidification, it follows that it must have a constant freezing-point, or, what amounts to the same thing, the solid mixture must have a fixed melting-point. That the above mixture is not a chemical compound, as is stated for similar cases by certain scientists, the above considerations amply show.

The solubility of the triphenylmethane at its "cryohydratic point" is so slight that the solution may truly be termed dilute, and the laws which have been established concerning dilute solutions are entirely applicable in this case. Thus it has been shown that the lowering of the freezing-point (Δt) of the solvent brought about by the presence of a dissolved substance with a molecular mass equal to M may be found by means of the equation

$$\Delta t = E\frac{m}{M},$$

where m represents the percentage composition of the solution and E the molecular depression of the freezing-point. At 3.9°, the freezing-point of the solution, it was ascertained that 100 parts of benzene dissolve 3.90 parts of triphenylmethane. Substituting these values in the above equation, we find $\Delta t = 0.799°$. The benzene employed melted at 4.73°, which is 0.83° higher than the point of fusion of the cryohydrate. This agrees within the limits of the unavoidable experimental errors with the value for Δt obtained by calculation.

Quite a general view is obtained of the states of equilibrium of the system, benzene and triphenylmethane, by a consideration of their solubilities. At 3.9° four phases are coexistent: 1. benzene (solid); 2. molecular compound of triphenylmethane and benzene (solid); 3. solution of triphenylmethane in benzene (liquid); 4. mixture of the vapors of benzene and triphenylmethane.

We have accordingly $n + 2$ phases of n chemical compounds and the temperature 3.9° marks a quadruple point of transition.

With rise of temperature phase 1., *i. e.* benzene (solid), disappears, and the system consists of but $n + 1$ phases until the temperature 37.5° is reached. Here the curve of solubilities changes abruptly. The curve up to this point has been almost a straight line but slightly inclined towards the axis of abscissæ. Now, however, it commences to rise more and more rapidly. This change in the direction of the curve indicates that some change must take place at 37.5°. As a matter of fact, this is the point at which the molecular compound of triphenylmethane and benzene decomposes into its constituent molecules. Above 37.5° the molecular compound is in labile, below that temperature in stable equilibrium. I have been unable to obtain solutions saturated with the molecular compound above 37.5°, so easily is it decomposed. Triphenylmethane does not, however, combine immediately and completely with benzene when introduced into it and kept at a temperature a little below 37.5°. Thus I have been able to obtain solutions of triphenylmethane at 35°–36°. At 37.5° a new phase comes into existence, *viz.* triphenylmethane (solid), and this temperature is another quadruple point of transition. The $n + 2$ coexistent phases are: 1. molecular compound of triphenylmethane and benzene (solid); 2. triphenylmethane (solid); 3. solution of triphenylmethane in benzene (liquid); 4. mixture of the vapors of triphenylmethane and benzene (gaseous).

Above 37.5° the solubility increases very rapidly until a temperature of 76.2° is reached, which is the melting-point of the molecular compound in closed tube. At this temperature the quantities of triphenylmethane and benzene are in molecular proportions, and solid trimethylmethane disappears. As the temperature now rises, benzene passes off rapidly as vapor, for its boiling-point is but 4° above this last point of transition. At 94.3°, the melting-point of pure triphenylmethane, the system loses benzene entirely and is reduced to a single chemical compound. 94.3° is accordingly a triple point of transition.

The system above studied is an excellent instance of the way in which the acts of solution and of melting pass continuously into each other. At 3.9° the cryohydrate melts; solution ensues, the solid being the molecular compound of triphenylmethane and benzene; at 37.5° this decomposes into its constituent hydrocarbons; at 76.2° complete fusion takes place, etc.

When benzene is added slowly to finely powdered triphenyl-

methane it is absorbed with evolution of heat. If the resulting dry mass be heated, it changes into a more or less viscous liquid at a certain temperature. If the benzene and triphenylmethane be mixed in molecular proportions, this occurs at 76°, the melting-point of the compound $CH(C_6H_5)_3 + C_6H_6$. If more benzene be added, however, liquidity takes place at lower temperatures. A homogeneous solution is not in reality obtained, but rather a suspension of the triphenylmethane in its solution. The temperature at which liquefaction takes place may be determined within a degree or so, as follows: The mixture, contained in a small Erlenmeyer flask, is heated in a glycerine-bath until it becomes liquid. The bath is then allowed to cool and the flask tilted so as to cause some of the solution to run upon the sides. On bringing the flask to a vertical position, so long as the mass is liquid it quickly runs down, while, if at all solidified, it does not move. By repeating this procedure several times the true temperature of solidification is obtained. In Table II are given the results of some determinations.

TABLE II.

Temperature.	$CH(C_6H_5)_3$ in grams.	C_6H_6 in grams.	Molecules of C_6H_6 to 1 mol. $CH(C_6H_5)_3$.	Solubility pts. $CH(C_6H_5)_3$ to 100 pts. benzene.
52°	4.88	5.50	3.52	36.92
45	4.88	6.37	4.08	23.04
17	4.88	8.29	5.31	6.98

An inspection of the table shows that the temperatures are functions of the solubilities. The explanation of the phenomena is obvious. For every temperature there is a minimum quantity of triphenylmethane which can be so disseminated throughout the solution that it deprives the latter in a measure of its mobility. As the solubility increases the temperature rises, the point at which liquefaction occurs rises also, since more of the solid triphenylmethane passes into the dissolved (liquid) state.

CHICAGO, *December* 19, 1892.

REVIEWS AND REPORTS.

The International Conference on Chemical Nomenclature.[1]

At the meeting of the International Chemical Congress, held in Paris in the summer of 1889, a special Section was appointed to consider the unification of chemical nomenclature, and, after discussing a variety of propositions, some of which were adopted, it was decided to form an International Commission for the further study of the subject.[2]

The members resident in Paris, having been constituted a permanent committee of the Commission, have devoted an immense amount of time and care to the preparation of a scheme, and it was to discuss their report[3] that we met at Geneva on Easter Monday last. The French Committee had issued invitations, not only to members of the Commission, but also to many other prominent chemists, so that the meeting was a thoroughly representative one. It is worth mentioning, as an illustration of the sympathetic treatment accorded by public bodies in France to men of science, that the Paris-Lyons-Marseilles Railway Company granted a reduction of one-half of the fare over their line to members of the Congress.

Very happily, the local committee had arranged that all might stay at the one hotel—the Métropole—and it was here that we first met in friendly union on the Monday evening.[4] The next

[1] Nature, May, 1892.

[2] The following chemists eventually consented to serve on the Commission: Messrs. Béhal, Berthelot, Bouveault, Combes, Fanconnier, Friedel, Gautier, Grimaux, Jungfleish, Schutzenberger (all representing France), Graebe (Switzerland), Alexejeff and Beilstein (Russia), von Baeyer and Nolting (Germany), Lieben (Austria), Paterno (Italy), Franchimont (Holland), Armstrong (England), Istrati (Roumania), Calderon (Spain), Cleve (Sweden), Boukowski Bey (Turkey), Ira Remsen (United States), and Mourgues (Chili).

[3] This report had been prepared by the following: Messrs. Friedel (President), Béhal, Bouveault, Combes, Fanconnier, Gautier, and Grimaux.

[4] The following is the official list of those who took part in the Conference: Messrs. H. E. Armstrong, Professor at the Central Institution, London, Secretary of the Chemical Society; A. Arnaud, Professor at the Museum, Paris; Adolphe von Baeyer, Professor at the University of Munich; Barbier, Professor at the Faculty of Sciences of Lyons; Aug. Béhal, Professor at the Superior School of Pharmacy of Paris; Louis Bouveault, Doctor of Science, Paris; Stanislas Canizzaro, Professor at the University of Rome; Paul Cazeneuve, Professor of the Faculty of Medicine of Lyons; Alphonse Combes, Doctor of Science, Paris; Alphonse Cosso, Director of the Experimental Station of Agriculture, at Turin; Maurice de Lacre, Professor at the University of Gand; Michel Filetti, Professor at the University of Turin; Emil Fischer, Professor at the University of Würzburg; A. P. N. Franchimont, Professor at the University of Leyden; Charles Friedel, Member of the Institute, Professor at the Sorbonne, Paris; Dr. J. H. Gladstone, F. R. S., London; Carl Graebe, Professor of the University of Geneva; Philippe-Auguste Guye, Professor at the University of Geneva; Istrati, Professor at the University of Bucharest; Albert Haller, Professor of the Faculty of Science of Nancy; Maurice Hanriot, Fellow-Professor of the Faculty of Medicine, Paris; A. R. Hantsch, Professor at the Polytechnic School of Zurich; Achille Le Bel, Doctor of Science, Paris; A. Lieben, Professor of the University of Vienna; Leon Maquenne, Doctor of Science, Assistant Naturalist at the Museum, Paris; von Meyer, Professor at the University of Leipsic; Denis Monnier, Professor of the University of Geneva; R. Nietzki, Professor of the University of Bale; Emilio Noelting, Director of the School of Chemistry of Mulhouse; Emmanuel Paterno, Professor at the University of Palermo; Amé Pictet, Instructor at the University of Geneva; William Ramsay, F. R. S., Professor of the University of London; Zdenko-H. Skraup, Professor of the University of Graz; Ferdinand Tiemann, Professor of the University of Berlin.

The Local Committee was composed of the following: Messrs. Emile Ador, H. W. de Blonay, Alex. Claparede, Prof. C. Graebe, Prof. Ph. A. Guye, Alex. Le Royer, Prof. Denis Monnier, Amé Pictet, Fred. Reverdin, Prof. Albert Rilliet, Edouard Sarasin.

morning the Congress assembled at the Hotel de Ville, M. Richard, the Cantonal Minister of Education, being in the chair. After an admirable address of welcome from this gentleman, who appeared to thoroughly appreciate the importance of the object in view, on the motion of Prof. Canizzaro it was wisely decided not to follow the complimentary, but somewhat unbusinesslike Continental practice so frequently adopted, of appointing a different chairman each day, but to have only one. M. Friedel, who had taken the chair at all the numerous meetings of the Paris Committee, having been chosen by acclamation President of the Conference, formal business was at once entered into, and, after the necessary interval for lunch, the sitting was resumed in the afternoon. We met in like manner on the two following days, and the final sitting took place on the Friday morning, but many had left before this. On Tuesday evening, by invitation of the local committee, we visited the theatre, a very beautiful building. On the Wednesday evening we were entertained by them at a dinner at the Hotel Métropole, on which occasion a very striking speech was delivered by Prof. von Baeyer, who, after pointing out that experimental chemistry had been carried, early in the century, into Germany from France by Liebig, who was tutored by Gay-Lussac, proceeded to say that, although the science had now undoubtedly reached its highest development in Germany, it was more than probable that, in the future, circumstances would arise which would lead to some other nation—France, Russia, Italy, or England—coming to the fore. On this occasion, on the motion of M. Le Bel, it was unanimously decided to appoint M. Marignac Honorary President of the Congress, and a letter to him expressing our regret that ill-health prevented his taking part in its work was at once signed by all present. We were indebted in many other ways to the local committee, and there is no doubt that the success of the meeting was in large measure due to the forethought and hospitable care exercised by them on our behalf. Absolute amity prevailed throughout, and it was clear that all were bent on co-operating to secure the carrying out to a successful issue of a very difficult but most important work. The great advantage to be derived from the personal intercourse which such meetings promote was soon apparent; gradually, the doubts which many entertained as to the possibility of devising a practical, rational scheme of nomenclature were dispersed, and ere many hours had elapsed the sympathies of all present were enlisted on behalf of the work; thus a mission has been sent forth which will explain the enterprise to chemists generally.

The resolutions passed at the meetings are appended to this article. These, I think, are in no way to be taken as in all respects final, but they will serve to prepare the way and to indicate the lines on which the work is to be carried out. The position in which we found ourselves placed, in fact, was not one which justified our arriving at decisions which could fairly be regarded as

binding. The report of the French Committee was placed in our hands only on the morning of the first meeting, and it was impossible to master its contents at so short a notice, and still less to criticise and test the application of its recommendations in detail. That the scheme would serve but as the basis for discussion was soon evident, when at the very outset a system of nomenclature for the hydrocarbons was adopted very different and far more significant than that recommended in the report; and numerous other departures from its recommendations were carried in the course of the proceedings. Again, some of the most active members of the Congress had confessedly paid attention only to special groups of compounds, and had not tested the application of proposals which they strenuously advocated to compounds of other groups; but as a nomenclature admirably adapted to one class may be open to all sorts of objections when applied to another, the general bearing of recommendations made with reference to special groups will have to be fully considered before they can be finally adopted. The resolutions relating to fatty acids (Nos. 18, 19) are of this kind, and their adoption was warmly opposed by an important minority on the ground that, however well they might be adapted to acids pure and simple derived from open-chain hydrocarbons, their application to acids derived from closed-chain hydrocarbons and acids containing other radicles in addition to carboxyl was beset with difficulty. In order to name an acid in accordance with this resolution, the formula of the corresponding hydrocarbon must be constructed from that of the acid by changing carboxyl into methyl; for example, citric acid, $CH_2(CO_2H).C(OH)(COOH).CH_2(COOH)$, would have to be regarded as a derivative of methylpentane, and would be named methylpentanoltrioic acid, numerals being adding to indicate the positions of the hydroxyl and carboxyl groups; in like manner, mellitic acid, $C_6(COOH)_6$, would be named hexamethyl-benzenehexoic acid, although no methyl is present in it. The mental effort involved in visualising the formulæ from such names as these would appear to be far greater than if they were respectively named propanoltricarboxylic acid and benzenehexacarboxylic acid, or simply propanoltri-acid and benzenehex-acid, the use of the term *acid* being understood to imply the presence of carboxyl. A decision on points such as these can only be arrived at after careful study of the general effect of such a proposal, and there was no time for such a comparison during the brief debate possible at a Conference. In some cases, there can be no doubt that the full force of objections raised to proposals in favor of which a majority subsequently voted was not felt, owing to the difficulty which necessarily arises at an international Conference if the language used be not equally familiar to all present, and consequently full expression cannot be given by all to their views. Moreover, although it is easy to criticise destructively even at short notice, constructive criticism under such circumstances is very difficult: consequently a proposal may be accepted even in face of serious

objections to its adoption simply because nothing better can be suggested at the time. An instructive case of the kind arose on discussing thio-compounds. The proposals in French report were not regarded as altogether satisfactory, and an amendment was suggested and carried which to many appeared most undesirable; the next morning, when the time came to confirm the resolutions arrived at on the previous day, the discussion was reopened, and a slight modification of the original proposal was suggested, which was recognised to be an improvement, and the objectionable resolution was rescinded. Clearly at such meetings much must depend on the right expression being found by happy inspiration at the right moment.

The one resolution which covers all others, and which defines the nature of the task to be undertaken, is the first. Whatever name we may choose to apply to a substance colloquially, it is clearly an absolute necessity of the times that every compound should bear a *systematic* name, of such a character that it can be at once translated into the corresponding formula; and that, *vice versa*, a name corresponding to any particular formula may be devised which we may count on finding in the *official* register, if the compound thought of have been described. The value of such a systematic nomenclature to original workers as well as to students cannot be overestimated, and few who are qualified to take part in such a work will grudge the time they may spend on it. There was considerable difference of opinion at the meeting as to whether a systematic nomenclature should be devised merely for the purpose of an official register, or whether the object aimed at should be a system of wider application; the majority, I believe, came to the conclusion that it should certainly subserve the one, but if possible both purposes. There can be little doubt, however, that the future student will cut the knot by declining to burden his memory with a double vocabulary in the case of all but the commonest substances, and that therefore there is but one course open to us (cf. Res. 26).

Although sufficiently conservative to retain methane, ethane, propane and butane, the Congress decided not to adopt the proposal to continue the use of the names formic, acetic, propionic, and butyric for the first four acids of the acetic series, which was advocated by a substantial minority, on the ground that their retention would facilitate the change from the old to the proposed new system. This is one of the questions demanding careful consideration. Many will, no doubt, prefer to retain old unsystematic names as far as possible, but it is easy to see that the desire to avoid change may carry us too far in this direction; it will undoubtedly be very inconvenient to the present generation of chemists to abandon familiar and cherished names, but nevertheless it may be a wise course to boldly face the difficulty, rather than inflict on coming generations a partially illogical and unsystematic nomenclature. The argument that the present familiar names

may still be used colloquially is, as I have already said, scarcely a justification of the dismissal of such names from the official nomenclature, as our successors may be expected to object more and more decidedly to a multiplex system as chemical science progresses, and to insist on the adoption of the official as the sole system ; the extent to which familiar trivial names shall be retained in the official system is therefore a matter of great importance.

As one aim and object must be to devise a system which is significant and logical throughout, no considerations must be allowed to prevail which will defeat this, and it will not suffice to quote present usage in support of illogical proposals; but this has been done. Thus the Congress decided (Res. 46) to name compounds of the type $R'.N_2.R'$ *azo*-compounds, while retaining the name *diazo*-chloride for $C_6H_5.N_2Cl$. It matters not to us that the manufacturers have chosen to call the colors derived from *diazo*-compounds azo-dyes; if substances such as $(C_6H_5)_2S$ are termed *thio*, and compounds such as $(C_6H_5)_2S_2$ *di*-thio compounds (Res. 43), we are bound to be consistent, and apply the significant term diazo to substances containing two nitrogen atoms. Resolution 46 ought therefore to be in part rescinded. I call attention to this case as an illustration of the tendency to break away from uniformity in favor of what may fairly be termed popular prejudice, which will require to be most carefully guarded against if the various sections of our system are to harmonise.

It will be gratifying to English chemists that the principle advocated for many years past by our Chemical Society, and enforced in its "Instructions to Abstractors"—that particular terminations should be regarded as indicative of particular functions, and should therefore be restricted to particular classes of compounds—has been legalised and extended by the Congress. This is a step of great importance, as we may expect that it will affect even trivial names, and that in future names will be given to new substances which will to a certain extent afford a clue to their nature; the hopeless confusion which now reigns supreme in the pages of the *Berichte*, for example, owing to the disregard of this principle by our German colleagues—who have hitherto been, as a rule, almost uniformly neglectful in matters of nomenclature—will, it may be hoped, ere long give way to more orderly treatment.

But the importance of applying this principle logically was not fully grasped even at the Congress, inasmuch as it was decided to affix the termination *ine* to acetylenic hydrocarbons, notwithstanding that this termination is admittedly indicative of basic properties. If, however, a suitable suffix ending in *ene* could be thought of, there would probably be little difficulty in securing its acceptance, in which case unsaturated hydrocarbons generally would have names ending in *ene*, and saturated hydrocarbons names ending in *ane*, and these terminations could be reserved exclusively for hydrocarbons.

It will be obvious from the foregoing remarks that although a

solid foundation for our future system of nomenclature has been laid, much remains to be done before a mature design, perfect in all its details, can be presented for adoption. At the meeting the hope was expressed that a decision might be speedily taken to enable Beilstein to utilise the proposals in the preparation of the third edition of his marvelous work; but it is clear that we are not yet so far advanced as to make this possible or even desirable, and it would be most unfortunate if Beilstein were at the present juncture to promulgate a system which is manifestly incomplete; nothing can be worse in such a case than to consent in haste, when it is evident that this would surely involve repentance at leisure.

Those of us who are interested in the work, and competent to advance it, must now test in detail the application of the proposals which have been provisionally adopted, and we must assist in contributing to the ultimate establishment of a system on the broad lines of policy laid down for our guidance at the Congress. As it is not improbable that in the future, owing to the extended use of our language, the major proportion of chemical students will speak English, it is essential that due attention be paid to the matter here in England, so that a system may be devised which we can make use of without difficulty.

Resolutions taken by the Congress.

1. In addition to the usual methods of nomenclature, an *official* name, permitting of distinguishing each body under a distinctive title, will be established. The Congress requests authors to mention in their articles the official name in parenthesis, in addition to the name chosen by them.

2. It is decided to consider, for the present only, those bodies of a known constitution, leaving for later consideration bodies of unknown constitution.

3. The termination *ane* is adopted for all the saturated hydrocarbons of the fatty series.

4. The old names of the first four saturated hydrocarbons (*methane, ethane, propane, butane*) are retained; the names derived from the Greek numbers will be used for those which have more than four atoms of carbon. These names will distinguish the normal hydrocarbons.

5. The hydrocarbons with an open chain are regarded as derivatives of the normal hydrocarbons, and their name will be derived from the longest normal chain that can be established in their formula.

6. The numbering of the lateral chains will be drawn from the atom of terminal carbon nearest in a lateral chain; in the case where the lateral chains nearest to the extremities will be placed symmetrically, the simplest will decide the choice.

7. Whenever a residue is substituted in a lateral chain, *metho-*, *etho-*, are employed instead of *methyl-*, *ethyl-*, prefixes reserved for the case where the substitution takes place in the principal chain.

8. In the hydrocarbons having only one *double bond*, the termination *ane* of the corresponding saturated hydrocarbon will be replaced by the termination *ene* (ex. ethene); in those having two *double bonds*, the termination *diene* will be used (ex. propadiene); those having three, *triene*, etc. If it is necessary, the place of the double bond is indicated by the number of the first atom of carbon to which this double bond is attached.

9. The names of the hydrocarbons with a *triple bond* will be terminated in like manner with *ine*, *diine*, *triine* (ex. ethine for acetylene, propine for allylene, hexadiine for dipropargyle).

10. In the case where occur simultaneously both *double* and triple bonds, the terminations *enine*, *dienine*, etc., will be employed.

11. The saturated hydrocarbons with a closed chain will take the names of the corresponding saturated hydrocarbons of the fatty series preceded by the prefix *cyclo* (ex. cyclohexane for hexamethylene).

12. The atoms of carbon in a lateral chain will be distinguished by the same number as the atom of carbon to which the chain is attached. They will carry a number which will indicate their distance from the point of attachment in the lateral chain.

In the case where two chains are attached to the same atom of carbon, the numbers of the most simple among them will be accented.

The same method of numbering is adopted for the lateral chains of the closed chains.

13. The non-saturated hydrocarbons will be numbered as the corresponding saturated hydrocarbons. In case of doubt or the absence of a lateral chain, the number 1 will be placed before the terminal carbon the nearest to the bond highest in order.

14. The numbering of the hydrocarbons is retained for all their substitution products.

15. The alcohols and the phenols will be called after the name of the hydrocarbon from which they are derived, terminated with the suffix *ol* (ex. pentanol, pentenol, etc.).

16. Concerning the polyatomic alcohols and phenols, one of the particles *di*, *tri*, *tetra*, etc., following the order of the polyatomicity, will be inserted between the name of the fundamental hydrocarbon and the suffix *ol* (ex. propane-triol for glycerin).

17. The name of *mercaptan* is abandoned, and this function will be distinguished by the suffix *thiol* (ex. ethane-thiol).

18. In the acids of the fatty series, the carboxyl will be considered as forming an integral part of the carbon skeleton.

19. The name of all the monobasic acids of the fatty series is derived from that of the corresponding hydrocarbon followed by the suffix *oic*.

The polybasic acids will be distinguished by the terminations *dioic*, *trioic*, *tetroic*, etc.

20. For the monovalent residues of the acids, the *oic* of the acid will be changed to *oyle*.

21. In the monobasic acids with the symmetrical or saturated normal chain, the carbon of the carboxyl bears the number 1.

22. The acids in which one or several atoms of sulphur replace as many atoms of oxygen of the carboxyl will be distinguished as follows: The sulfur simply united with an atom of carbon will be designated by the suffix *thiol;* if the bond is double, the suffix *thion* will be used. Examples:

$CH_3.CO.SH.$	Acid-ethane-thiolic.
$CH_3.CS.OH.$	Acid-ethane-thionic.
$CH_3.CS.SH.$	Acid-ethane-thionthiolic.

23. The Congress gives its adhesion to the following proposition, without expressing a definite vote on the subject:

The oxy-ethers will be designated by the names of the hydrocarbons which compose them, united by the term *oxy-* (ex. pentane-oxy-ethane for ethyl or amyl oxide).

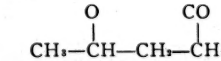
24. The anhydrides of the acids will retain their present mode of designation after the name of their acids (ex. anhydride ethanoic).

25. (12 *bis.*) In the case of two lateral chains attached to the same atom of carbon, the order in which these are expressed will correspond to their degree of complication.

26. A more exhaustive discussion of the bodies with complex functions is postponed, and the study of this question is referred to the International Commission, in order that it may prepare upon this point a plan which will be laid before the next Congress. The Commission will endeavor to reconcile the exigencies of the spoken nomenclature with that of a terminology applicable to the dictionaries.

27. The customary methods for the salts or compound ethers are retained.

28. The lactones will be designated by the word *olide*, indicating that it is an internal anhydride of alcohol and acid. The position of the alcoholic function, as to the carboxyl of the acid alcohol whence proceeds the lactone, can be expressed by the Greek letters α, β, γ, δ, in addition to the usual numbering of the lateral chains:



1.4 pentanolide or 1.4 γ pentanolide.

29. The lactonic acids derived from bibasic acids will be named after the lactones from which they are derived, adding the suffix *oic*, characteristic of the acids.

30. The discussion of the closed chains is postponed until the publication of the ideas of Mr. Armstrong upon this subject, will permit the International Commission to compare them with the propositions of Mr. Bouveault.

31. In the aromatic series and all the bodies containing a closed chain, all the lateral chains will be considered as substituting.

32. Aldehydes will be distinguished by the suffix *al* (methanal, ethanal).

Sulfo aldehydes: suffix *thial.*

33. Acetones: suffix *one* ($CH_3.CO.CH_2.CH_3$, butanone 2).

Diacetones, triacetones: suffixes *dione, trione.*

Sulfoacetones: suffix *thione.*

34. Quinones: The suffix *quinone* for the bodies homologous to ordinary quinone.

The bodies having the chain CO.CO several times will be diquinones or triquinones.

35. Ammoniacal compounds: no change (ex. ethylamine, ethene-diamine).

The bodies where the bivalent group—NH—closes a chain formed of positive radicles will be called *imines* (ex. ethene-imine).

Phosphines, arsines, stibines, sulphines: the nomenclature in use is retained.

36. Hydroxylamine: this name is retained.

37. Oximes: will be designated by following the rules at present admitted: the *isonitroso* bodies will be called oximes.

(Ex. $CH(NOH).CH_2.CH_2CH_3$ 1 Butanoxione.
$CH_3.CH_2C(NOH).CH_3$ 2 Butanoxime.)

38. Amides: this name is retained (ex. ethanamide.

$NH_2.CO.CH_2.CH_2.CO.NH_2$ Butanes diamide.
$COOH.CO.CH_2.CH_2.CO.NH_2$ Butanamidoic acid).

Imides: will be retained.

Amidoximes: this name will be retained.

(Ex. $CH_3.C(NOH).NH_2$ Ethanamidoxime.)

Urea: the generic word *urea* will be retained, and will be employed as a suffix for the alcoholic derivatives of urea, while the derivatives from an acid substitution will be called *ureides.*

The bodies containing two molecules of urea will be distinguished by the suffixes *diurea, diureide.* The acid ureides will take the name *ureic acids.* The terminations *uramic* and *uric* are abandoned.

39. Amidines: this suffix will be retained.

(Ex. $CH_3.C.NH.NH_2$ Ethanamidine.)

For the derivatives the name will be doubled, and the name of the substituting group will be preceded by, either amino, or amidine, as the case may be.

(Ex. $CH_3.C(NC_2H_5).NH_2$ Ethanamino ethylimidine.
$CH_3.C(NH).NHC_2H_5$ Ethanethylamino-imidine.)

Guanidines: the generic word *guaniaine* is retained, but different guanidines will be named as substitution derivatives of diamido-carbo-imidine.

40. Betaines: suffix *taïne.*

(Ex. $N(CH_3)_3$—O Ethanoyltrimethyltaine).

CH_2———CO

41. Nitriles: the question is left in suspension for the fatty series. The prefix *cyano* (as a name of the substituting body) is adopted for the aromatic series.

42. Carbylamines: the nomenclature in use is retained.

43. Sulfones: this name is retained.

(Ex. $C_6H_5.SO_2.C_6H_5$ Benzene-sulfone-benzene).

Sulphides: will be designated by putting *thio* between the two saturated components (provisionary decision).

(Ex. $C_6H_5.S.C_6H_5$ Benzene-thio-benzene).

Disulfides: will be designated in the same manner by *dithio.*

44. Isocyanic ethers: suffix *carbonimid.* Ex. The ethyl cyanate of Wurtz will be called ethylcarbonimid. The corresponding sulfo-derivative will be called in the same manner ethylthiocarbonimid.

Cyanates: this name is retained for the true ethers which, by saponification, give cyanic acid or its direct product of hydration. The name sulfocyanate will be replaced by *thiocyanate.*

45. Nitro bodies: the nomenclature in use is not changed.

46. Azo bodies: the terms *azo* and *diazo* are retained, but the mode of enunciating these compositions will be modified as follows:

(Ex. $C_6H_5.N_2.Cl$ Diazobenzene chloride.
$C_6H_5.N_2.C_6H_5$ Benzene-azo-benzene.
$C_6H_5.N_2.C_6H_4.N_2.C_6H_5$ Benzene-azo-benzene-azo-benzene).

HENRY E. ARMSTRONG.

THE MAGNETIC ROTATION OF COMPOUNDS SUPPOSED TO CONTAIN ACETYL, OR TO BE OF KETONIC ORIGIN.

A few years ago a review of some work by W. H. Perkin on the relation between chemical composition and magnetic rotation appeared in this Journal.[1] Since then Mr. Perkin has been engaged principally in studying the effect of variation of chemical constitution on magnetic rotation, and in a paper which has just been published[2] he submits the evidence obtained by the application of this physical method to the determination of the structure of that much investigated compound, ethyl acetoacetate. The principal results are given below.

No definite relationship between chemical composition and magnetic rotation was discovered until 1882, as the method of calculating the experimental results consisted in comparing the magnetic rotatory effect of unit lengths of liquids. Mr. Perkin says: "If unit lengths of vapor could be examined, some useful information might be obtained, because these lengths would contain the same number of molecules." On account of the experimental difficulties of determining the rotation produced by gases, he examined the magnetic rotation per unit length of liquids,

[1] This Journal **6**, 356. [2] J. Chem. Soc. **61**, 800–864.

and attained the same end by referring the results of the observations to the lengths of columns of liquid which would be formed by the condensation of unit lengths of vapor. The lengths compared were thus directly proportional to the molecular weights and inversely proportional to the densities of the two liquids, and the ratio of the rotations produced by such lengths of the substance under examination and of the standard substance when placed in the same magnetic field, is called the *molecular magnetic rotation.* The quantity thus defined was found to depend not only upon the composition of the molecule but also upon its constitution.

The effect of composition is illustrated in any series of similarly constituted compounds. A constant difference in composition of successive members corresponds to a constant difference in their molecular magnetic rotation. Thus, in the series of normal hydrocarbons, to the constant difference in composition CH_2, corresponds the constant difference in molecular magnetic rotation 1.023. Moreover, a difference in composition of CH_2 produces this same difference of molecular rotation in the other homologous series. In general, a number can be found for every homologous series which, when increased by 1.023 times the number of carbon atoms in a given member of the series, will give its molecular rotation. This number is called the *series-constant* and varies with the constitution, being different even for the series of primary and secondary alcohols. For the series of normal hydrocarbons the series-constant is 0.513. To obtain the rotation of hexane we add to this 6×1.023, and the sum, 6.651, agrees very well with the molecular rotation actually observed, 6.646.

In determining the chemical constitution of a compound, its chemical behavior will usually limit the number of possible formulæ which might be applied to it. Thus, in the case of ethyl acetoacetate, only two formulæ can be considered:

(1) $CH_3.CO.CH_2.COOC_2H_5$, and
(2) $CH_3.C(OH)=CH.COOC_2H_5$.

Both agree more or less closely with its chemical conduct. According to one of these formulæ, the compound is unsaturated; according to the other, it is plainly a saturated ketone.

The molecular rotatory power of saturated compounds is, however, much smaller than that of the corresponding unsaturated compounds. By a determination of the molecular rotation of ethyl acetoacetate it should therefore be possible to determine which of the two formulæ above is the correct one.

This was done some years ago, and the value obtained agreed very well with that calculated on the basis of formula 1. Accordingly formula 1 was adopted, and now Perkin examines the rotation of a large number of other acetyl derivatives, in some of which there can hardly be any other than a ketonic structure, to test the validity of his conclusion.

Among the substances examined were the following:

Pyruvic acid, $CH_3.CO.COOH$.—This substance could hardly have any other than the above structure. The molecular rotation observed agreed with that calculated on this assumption.

Ethyl acetoacetate.—The molecular rotation was examined at 16° and at 90°, and was found to agree approximately with that calculated on the basis of the ketonic formula. At the higher temperature the rotation is somewhat less and indicates, if anything, that any small amount of the unsaturated isomer which might be present at the lower temperature is decreased; so that at higher temperatures the substance would probably act more like a ketone and less like an unsaturated compound than at lower temperatures.

Ethyl ethylacetoacetate, $CH_3CO.CH.C_2H_5.COOC_2H_5$. — This substance was examined so that a comparison could be made with ethyl ethylmalonate, in which case there is no possibility of a hydroxy structure. The difference between the molecular rotations of ethyl ethylacetoacetate and ethyl acetoacetate was the same as the difference between those of ethyl ethylmalonate and ethyl malonate, indicating that the replacement of ethyl is analogous in both cases. In ethyl ethylmalonate it is directly in combination with carbon.

Ethyl allylacetoacetate, $CH_3.CO.CH(CH_2.CH:CH_2).COOC_2H_5$. — This was examined on account of its unsaturated condition, and the molecular rotation indicated the presence of only one double bond in the compound.

Levulinic acid, *β-Acetopropionic acid*.—The molecular rotation agreed with the ketonic formula, $CH_3.CO.CH_2.CH_2.COOH$. The acid was examined because it was thought that it might be more capable than the ethereal salts of changing to the hydroxy form, $CH_3.C(OH):CH.CH_2.COOH$.

Ethyl acetonedicarboxylate.—This is ethyl acetoacetate with a hydrogen atom of the acetyl group replaced by a negative group, *viz*. $COOC_2H_5$. The rotation observed was found to be slightly high at ordinary temperatures, indicating the presence of some of the hydroxylic isomer. On re-examination at 94°, the rotation agreed very well with that calculated from the ketonic formula. Perkin thinks that at ordinary temperatures some of the hydroxy isomer is present, due to the influence of the negative group $COOC_2H_5$.

Diketonic compounds.—A number of these were examined. Besides a monohydroxy isomer there is here also the possibility of a dihydroxy isomer. Thus acetylacetone might have any one of the following structures:

(1) $CH_3.CO.CH_2.CO.CH_3$,
(2) $CH_3.C(OH):CH.CO.CH_3$,
(3) $CH_3.C(OH):C:C(OH).CH_3$.

The interest attached to the examination of this compound arises from the fact that the molecular rotation observed at ordinary temperatures was very large, indicating it to be a hydroxy unsaturated compound with about 20 per cent. of the isomeric dihydroxylic compound. At 93° the rotation corresponded to that of a mixture of the diketonic and hydroxyketonic compounds. When cooled it quickly regained its original rotation.

The methyl derivative showed a much weaker tendency to pass over into its hydroxylic isomers, and the ethyl derivative showed this tendency in a still smaller degree. The methyl derivative passed readily into the diketonic modification on heating to 90°, but retained its constitution for some time after it had cooled, as was shown both by its molecular rotation and its density.

The examination of the molecular refraction and dispersion, which also enables us to distinguish between saturated and unsaturated compounds, led to similar conclusions, and it may be said here that, wherever both the magnetic rotation and refraction and dispersion of a compound have been examined, the results obtained by the one method are in strict accordance with those obtained by the other.

Triketonic compounds.— The only one examined, diacetylacetone, was found at 60° to consist of the dihydroxylic isomer. The constitution also changes with the temperature.

The existence of products consisting of two or more isomeric compounds side by side, their relative proportions varying with the temperature, is remarkable and may have, as Mr. Perkin says, something to do with the way these products behave in different reactions.

He intends to examine mixtures of some of these compounds with different reagents, as this might show whether the relative proportions of the isomers present are dependent on the reagent used. The results of such an investigation will be awaited with much interest.

F. A. Wolff, Jr.

A List of the More Important Changes in the Spelling and Pronunciation of Chemical Terms, recommended by the American Association for the Advancement of Science, with the Reasons therefor.

Elements.—*Aluminum* is spelled in the shortened form in deference to the wishes of technical chemists, on account of the growing importance of the metal in manufactures.

Cesium loses the *a* of the diphthong, as unnecessary, while the new form is in harmony with the French and Italian orthography.

Columbium replaces *Niobium* as a matter of historical justice. It was called columbium by its discoverer.

Glucinum is preferred to *Beryllium* on the same ground of historical priority.

Sulfur is modified in accordance with the general phonetic simplification going on in our language. The new form brings us into accord with the French, German and Italian usage. The replacement of **ph** by **f** is carried out in all the derivatives. (It has not been deemed advisable to yield at present to the wish of many, that a similar change should be made in the spelling of phosphorus, as the German and French languages still retain the **ph**.)

The termination **-ic**.—This is used for metals only when there is a contrast with **-ous**, thereby avoiding several non-euphonious terms, and bringing us into accord with the British custom. Thus avoid aluminic, zincic, strontic, etc.

The termination **-ol**.—This is used exclusively for alcohols, and and all alcohols receive the termination. This also is in harmony with British usage, and brings about a most desirable simplification and uniformity. Thus, glycerol, quinol, etc.

Terminations in **-id**.—The final **e** is dropped from all chemical terms formerly ending in **-ide**, and the pronunciation is always -ĭd.[1] Of the three pronunciations of this termination— -īde, -ĭde, and -ĭde—in varying degrees of use amongst us, the second appeared undoubtedly the most preferable for the following reasons: -īde is an uncommon, almost unnatural pronunciation of the vowel in our language, although it would bring us into unison with European usage and simplify phonetic values for the ears of foreigners; -īde leads frequently to confusion with -īte (sulfīde and sulfīte) and is the value of **i** farthest removed from European usage; -ĭd approximates closely to the continental ĭd, —into which it is easily lengthened,—is readily recognised by the foreign ear, is not confused with termination -īte, is in line with present phonetic progress, and has the backing of authority and usage. The short sound of **i** naturally dictates the dropping of the final **e**. ("According to Smart and Cull, chemical terms ending in **-ide**, as bromide, chloride, etc, should be pronounced with **i** long; but all other orthoëpists are unanimous in making the vowel short; and the propriety of the latter mode of pronunciation is established by the fact that this whole class of words is not unfrequently spelt without the final **e**; thus bromid, chlorid."—Webster's Dictionary, edition of 1864 and 1884, Principles of Pronunciation, p. xliv.)

Terminations in **-in**.—In the names of chemical compounds, including all those formerly ending in **-ine** (except the small group of doubly unsaturated hydrocarbons, as propine), this termination is always pronounced -ĭn and is never followed by an **e**. In this case much the same reasons as those given in the preceding paragraph dictate the uniform use of -īn, and not only authority, but modern usage is even more fixed in the employ-

[1] Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marine, nōte, nŏt, mōve, tūbe, tŭb, rüle, mÿ, ў = i.

ment of the short **i**, so much so that the change practically amounts to simply dropping the final **-e** when following **-in.** The only objection to be raised against the innovation is that based on the recommendation of Watts some few years since, that basic substances should terminate in **-ine** and neutral substances (*viz.*, glycerids, glucosids, proteids, and bitter principles) in **-in.** While this distinction possesses a certain value, it is to be noted that it involves a difference in spelling with little or no difference in pronunciation—a useless and undesirable complication, and out of touch with modern phonetic principles; it demands a very extensive knowledge of the constitution of a large number of compounds with these terminations; it has never been recognised by many chemists; and, finally, while it has been partially adopted by others it has rarely been used consistently.

Terminations in **-meter.**—Words in this class used in the metric system are regarded as compound words, and each portion retains its own accent; as mil'lime″ter.[1] Of the two authorised forms of accentuation, it was deemed better to retain this and exclude completely the other (*viz.*, the uniform laying of the accent on the antepenult), because the former is of help to foreigners using our language and *vice versa*, while the practice accords with the general rule for the retention of the primitive accents in compound words.

Derivatives of *Valence.*—The Latin prefixes are used invariably to the exclusion of the Greek, in accord with the recognised principles of word-building in our language.

Arsin, Stibin, Phosphin, Hydrogen Sulfid.—These shorter terms, long since adopted by many chemists, now supersede completely the cumbersome arsenuretted hydrogen, etc. (It is to be hoped that the simplification may soon be carried a step further bythe introduction of sulfin, selenin, and tellurin.)

Gramme.—The retention of the **-me** of the French spelling may seem ill to accord with principles of phonetic reform actuating many of the above changes. It is, however, dictated by reasons of prudence, so long as the metric system is used side by side with the old apothecaries' series of weights and measures by our physicians and pharmacists. When the transition-period is over, and the latter system is effectually displaced, the simpler form will unquestionably be adopted. It is obvious to all that the marked similarity in sound and spelling between the words *grain* and *gram* could easily lead to mistakes of the gravest nature, and as a matter of fact a number of deaths have already been caused by either mere inadvertence or by the omission of the dot over the *i* in *grain.* (*Amer. Druggist*, **20**, 369.)

The following quotation from an article by Professor Edward Hart, in the Journal of Analytical and Applied Chemistry, is of interest in connection with the above:

[1] Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

"These proposed changes were carefully canvassed with those gentlemen who have made the English language their life-study and who were unanimous in favor of them. They were made the subject of a number of reports to the American Association for the Advancement of Science and were favored by a large majority of those present. In drawing up the report the committee sought and obtained the opinions of a number of chemists not members of the Association, and so far as it was possible to obtain an expression of opinion the recommendations voice the wish of American chemists."

In the article from which this quotation is taken occurs the passage: "Man is a conservative animal and does things in a certain way because he is accustomed so to do them. This conservatism increases with age until it becomes almost impossible to shake it off." In the face of these fundamental truths one hesitates to express an opinion on the recommendations of the American Association, fearing that to differ may be to proclaim one's self an ass, and the ass is even more conservative than man. This spelling, as every one knows, is a hard subject to deal with, and the Committee of the American Association deserves much credit for the care they have given to their work. Their recommendations seem on the whole to be wise, and it would perhaps be well if every chemist would adopt them. There is one chemist known to the present writer who is willing to acknowledge that he doesn't like "sulfur," but he is also willing to acknowledge that this is no argument against it.

One of the advantages which the committee mention under the head of **-ic** is "bringing us into accord with the British custom"; and their recommendation as to **-ol** "also is in harmony with British usage and brings about a most desirable simplification and uniformity." If conformity to British usage be advantageous, then why, it may be asked, should we be advised to fly directly in the face of British usage by dropping the final **e** "from all chemical terms formerly ending in **-ide**"? **-id** may be just as good as **-ide**, but is not uniformity worth much? Then, again, **-ine** has been growing in favor of late years as signifying basic properties, and it seems to the writer that in contracting to **-in** we lose more than we gain by giving up the **-e**. Perhaps a joint committee of the British Association and American Association might reach some conclusions of value. The question as to the use of the final **-e** is, however, one that will not be settled by any committee.

I. R.

THE ACTIVE COMPONENTS OF INACTIVE LACTIC ACID.

In 1884 Lewkowitsch[1] stated that a solution of ammonium lactate becomes dextro-gyratory after having been subjected to the action of *Penicillium glaucum*. The work of Linossier, pub-

[1] Ber. d. chem. Ges. **16**, 2720.

lished in 1891,[1] was a repetition and extension of that of Lewkowitsch, but led him to the conclusion that the salt solution becomes laevo-gyratory through the action of the ferment, and that from this solution a dextro-gyratory lactic acid can be obtained. On the other hand, Schardinger[2] obtained a laevo-gyratory lactic acid by the bacterial decomposition of cane-sugar. This acid formed a zinc salt of the same composition as that of sarcolactic acid, and when these two salts were mixed in equal quantities in solution it was found that ordinary zinc lactate crystallised out. It remains for us now to notice that Purdie and Walker[3] have succeeded in separating, by means of the strychnine salts, the two active varieties of lactic acid from the inactive variety, and have shown that they possess equal and opposite optical activity.

In experimenting with alkaloid salts, cinchonine and narcotine were employed with little or no success. On the other hand, on fractional crystallisation of a neutral solution of strychnine in pure lactic acid, salts were obtained which in solution exhibited optical activity. The least soluble salt was dextro-rotatory; from this a laevo-rotatory acid was set free, and from this in turn the zinc salt was prepared. This last should possess, according to analogy, the same composition and chemical properties as the well known zinc sarcolactate. The composition of the two was in fact shown to be identical, and to differ from that of the ordinary zinc lactate in containing one less molecule of water. The solubility of zinc laevo-lactate in water was shown to be practically identical with that of the sarcolactate; the same statement may be made with respect to their respective rotatory powers.

An examination of the free laevo-lactic acid showed that, like sarcolactic acid, this acid rotates the plane of polarisation in one direction, while its salts rotate it in the other. Like sarcolactic acid, it readily forms an anhydride whose activity is in the opposite sense to that of the acid. The acid was shown to be identical with Schardinger's.

From the more soluble strychnine lactate crystals a zinc dextro-lactate was prepared identical with zinc sarcolactate; from this salt sarcolactic acid could be isolated.

From the two lactic acids thus obtained, isomeric zinc-ammonium salts were prepared, alike in all but the direction of their optical activity.

A confirmatory experiment was made as follows: Equal weights of the two active zinc salts were mixed in solution, and pure, absolutely inactive zinc lactate crystallised out. W. W. R.

[1] Bull. Soc. chim. (Paris), [3] **6**, 10; Abstr.—Ber. d. chem. Ges. **24**, (c) 660.
[2] Monatsh. Chem. **11**, 545; Abstr.—This Journal **13**, 277; J. Chem. Soc. **60**, 666.
[3] J. Chem. Soc. **61**, 754.

COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, etc., with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By ALFRED H. ALLEN. Second Edition, Revised and Enlarged. Volume III, Part II.—AMMONIUM BASES, HYDRAZINES, BASES FROM TAR, VEGETABLE ALKALOIDS. Philadelphia: P. Blakiston, Son & Company. viii & 584 pp. 8vo. $5.00.

As every chemist knows, there is no better book than Allen's on the subject of Organic Analysis. It is a necessity in every chemical library. Every addition is welcome, and this new volume is specially welcome because it treats of specially important subjects. In the Preface the author says: "It is ten years since the publication of the last edition of that part of COMMERCIAL ORGANIC ANALYSIS which treated of Alkaloids and Tar Bases. These subjects then occupied about 120 pages. In the new edition now issued 570 pages have already been printed, and I feel reluctantly compelled to publish the subject-matter now ready as PART II of VOLUME III, leaving the sections on the less important ALKALOIDS and the chapter on ANIMAL BASES, CYANOGEN COMPOUNDS, PROTEIDS, etc., to be issued separately as Part III.

"In PART II, now published, I have endeavored to describe fully and accurately such of the Organic Bases as have any practical interest, and to give reliable information as to their sources. The AMINES, HYDRAZINES, and PYRIDINE and its Derivatives are now considered for the first time. The ANTIPYRETICS and other synthetical remedies with which modern chemistry has enriched medicine, are described fully in cases where they fall appropriately within the scope of the present volume; and I believe the sections on Antipyrine, Antifebrin, Phenacetin, Thalline, etc., contain a résumé of all published information on their respective subjects. In the chapter on VEGETABLE ALKALOIDS I have spared no pains to render the more important articles as complete and trustworthy as possible. . . .

"In the sections on TEA, COFFEE, and COCOA, which conclude the volume and together occupy 73 pages, I have incorporated nearly every item of trustworthy information of a chemical nature within my knowledge, and I believe these articles will be found of service by many besides professional chemists.

"PART III, completing the work, will be published as soon as possible, and will, I hope, be followed at no distant date by a new edition of the earlier volumes."

The book appeals to the chemist who is devoted to the pure science almost as strongly as to him who is mainly in search of analytical methods. The treatment is thoroughly scientific. There is nothing of the rule-of-thumb about it. The author from long experience in the laboratory knows what the analyst will want to know, and tells him this clearly. He also, undoubtedly,

tells him much that will have no "practical" value, and some of this will, perhaps, look strange and uninviting; but this will be of special value to many, and of some value even to those who do not understand it, for it is well for us all at times to be forcibly reminded of our own ignorance.

There are some interesting revelations as regards adulterations of coffee and tea. Magnetic iron ore and brass-filings are among the pleasant things mentioned as adulterants of tea. Under coffee we are told of all sorts of things, and this passage is not surprising: "The diminished consumption of coffee in England is doubtless largely due to the frequency and extent of its sophistications."

I. R.

CHEMICAL LECTURE EXPERIMENTS; NON-METALLIC ELEMENTS. By G. S. NEWTH, Chemical Lecture Demonstrator in the Royal College of Science, South Kensington. Longmans, Green & Co., London and New York, 1892. vi & 320 pp. 8vo.

Here is a book that will bring joy and consolation to many. It is unquestionably an improvement, and a great improvement, upon its predecessors. On almost every page even the experienced lecturer will find something suggestive, either an old experiment in new form or a new experiment. It is certain that of the experiments many will be new to some and some will be new to many. The descriptions are clear and give one confidence; and the drawings of apparatus are all new "with the exception of three." They represent apparatus actually used to-day, not antiquated forms. This use of new drawings gives the book a fresh appearance and lures one on to read, and the more one reads the better he is pleased. The author tells us that "no account of any experiment has been introduced into the book upon the authority solely of any verbal or printed description, but every experiment has been the subject of my personal investigation."

While primarily intended for teachers, the book will also be found useful by students. In what way, can best be indicated by the author's own words. "Secondly," he says, "it is my object to furnish the chemical student with a book which shall serve as a companion to the lectures he may attend—a book in which he will find fully described most, if not all, of the experiments he is likely to see performed upon the lecture-table, and which will therefore relieve him from the necessity of laboriously noting them and often sketching the apparatus used. In this way the student will be spared much unnecessary and distracting work during the lecture, and will therefore be better able to give his undivided attention to the explanations or arguments of the lecturer."

The "wire-gauze spoon" method of collecting hydrogen from the action of sodium upon water is gone, it is to be hoped never

to return. In its place a simple and ingenious device appears which deserves to be widely known, as it will contribute to the peace of mind of many lecturers. The author says it "is the best method, and the only one which is free from danger." It is thus described: "A piece of ordinary lead or composition pipe, about 25 millimetres long and about 4 millimetres bore, has one end closed by squeezing in a vice, or by a few taps with a hammer. A pellet of sodium is rolled between the fingers and pushed into this tube. It may well be forced in by pressing the mouth of the tube down upon the table, the excess of the metal being afterwards trimmed off with a knife. This tube with its contents is then dropped into the pneumatic trough, in which it will sink, and hydrogen will be evolved in a steady and gentle stream. . . . If the little tubes are filled as described, it is impossible for any explosion to take place in the performance of this experiment. The filled tubes may be preserved in naphtha." A detailed description of the method of sealing bulbs containing a mixture of hydrogen and chlorine is given, and no doubt many will be glad to get this information. Among the many other good experiments presented the following may be specially mentioned: one showing the combustion of ammonia in oxygen; the liquefaction of ammonia by cold and pressure; freezing water by solid mercury; the preparation of nickel carbonyl, $Ni(CO)_4$; many experiments on flames, etc., etc.

Excellent instructions are given in connection with many of the experiments for the use of the lantern; and a special section of the book is devoted to "Lantern Illustrations." In an "Appendix," finally, a number of valuable tables are given. I. R.

THE CHEMICAL BASIS OF THE ANIMAL BODY.—An Appendix to Foster's Text-Book of Physiology. Sixth Edition. By A. SHERIDAN LEA, University Lecturer in Physiology in the University of Cambridge. New York and London: Macmillan & Co., 1893. 288 pp. 8vo.

While this book is chiefly interesting to physiologists, chemists who wish to inform themselves concerning the substances that enter into the composition of the animal body will find it of value. The trouble with most books of the kind is that they bear unmistakable evidence of having been written by physiologists whose knowledge of chemistry is deficient. But in the present case we are informed that the author is "indebted to Dr. S. Ruhemann for reading the proofs from page 91 to page 216, in which the text contains many formulae, and involves special chemical knowledge." As Dr. Ruhemann is a chemist, the result is that the book is free from chemical solecisms, and the chemist can read it without having his prejudices stirred up. Due attention is given to the researches of Emil Fischer in the sugar-group, to the

conceptions of stereo-chemistry as illustrated in the lactic acid group, and to the constitution of uric acid and related substances. Of course, the rôle played by chemical substances in the body is the point of interest to the physiologist, and the results of investigations bearing upon this subject appear to be well summed up. A good example of this is found under urea. First, the chemistry of this compound and its most important derivatives is given; then, analytical methods applicable to it; then, the methods of synthesis; and, finally, a full discussion, based upon established facts, of the part played by urea in the body. Wöhler's epoch-making discovery of the conversion of ammonium cyanate into urea acquires new interest in the light of the following remark: "In other words, ammonium cyanate is a type of living, and urea of dead nitrogen, and the conversion of the former into the latter is an image of the essential change which takes place when a living proteid dies." The meaning of this sentence is not, to be sure, quite clear without the context. With this, it is highly suggestive. As regards the importance of chemical study to the physiologist the author says: "The physiological function of any substance must depend ultimately on its molecular (including its chemical) nature; and though at present our chemical knowledge of the constituents of an animal body gives us but little insight into their physiological properties, it cannot be doubted that such chemical information as is attainable is a necessary preliminary to all physiological study." I. R.

BERZELIUS UND LIEBIG. Ihre Briefe von 1831-1845 mit erläuternden Einschaltungen aus gleichzeitigen Briefen von Liebig und Wöhler sowie wissenschaftlichen Nachweisen herausgegeben von JUSTUS CARRIÈRE. 1893. München und Leipzig: Lehmann. vii und 280 pp. 8vo.

It is fortunate for the chemical world that in the early part of this century letter-writting was not a lost art and that value was attached to letters. For the chemist, there is hardly a more interesting book than that which a few years ago brought before us the letters of Liebig and Wöhler. And now we have another treat in this small volume of the letters of Liebig and Berzelius, which we owe to a grandson of Liebig who began at an early age to collect letters for the sake of the autographs. Anything written by these great men in regard to their work must be read with interest and profit by the present generation. This is the very heart of history, and one feels it throb as one reads. I. R.